

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JUNE, 1932.



General, Physical, and Inorganic Chemistry.

- Magnitude of spectral lines of stellar hydrogen.** P. ROSSIER (*Arch. Sci. phys. nat.*, 1932, 14, 5—23).—Using a spectrocomparator, the relative and abs. magnitudes of the lines of stellar H_2 as a function of the length of the spectrogram are plotted and interpreted from an examination of more than 400 spectrograms relating to a similar number of stars. N. M. BLIGH.
- Lower energy levels of the carbon atom.** N. F. BEARDSLEY (*Physical Rev.*, 1932, [ii], 39, 913—921).—Mathematical. Approx. calculations are compared with experimental data. N. M. BLIGH.
- Mechanism of the positive column in monoatomic gases. II.** R. SEELIGER (*Physikal. Z.*, 1932, 33, 313—327). A. J. MEE.
- Energy balance in the positive column in rare gases.** K. SOMMERMEYER (*Ann. Physik*, 1932, [v], 13, 315—336). A. J. MEE.
- Luminosity of a flame containing sodium vapour.** T. W. BONNER (*Physical Rev.*, 1932, [ii], 40, 105—111).—The luminosity of a flame into which a Na salt is sprayed is a function of the product of the thickness of the flame and the concn. of the Na in it (cf. A., 1928, 449; 1931, 1210). N. M. BLIGH.
- Arc spectrum of phosphorus.** C. C. KIESS (*Bur. Stand. J. Res.*, 1932, 8, 393—401).—Using infra-red sensitised plates, the P arc spectrum has been photographed in the near infra-red region, and about 400 wave-lengths have been measured over the range 9100—10,800 Å. These have been classified as combinations between quadruplet and doublet terms, all required theoretically for the P atom. From the series-forming terms the val. of the lowest term $4S_{11}^0$ is 90,000 cm^{-1} ; ionisation potential 11.11 volts. J. W. SMITH.
- Arc discharge not obtained in pure argon.** G. E. DOAN and J. L. MYER (*Physical Rev.*, 1932, [ii], 40, 36—39).—In highly-purified A an arc could not be struck between pure Fe electrodes. Explanations of the apparent dependence of the normal arc discharge on the presence of chemically active atoms or mols. are discussed. N. M. BLIGH.
- Zeeman effect of the K II spectrum.** A. E. WHITFORD (*Physical Rev.*, 1932, [ii], 39, 898—904).—Anomalies of classification are investigated and explained. A special press for feeding an arc with K metal is described. N. M. BLIGH.
- Band spectra of calcium hydride. II.** B. GRUNDSTRÖM (*Z. Physik*, 1932, 75, 302—312).—The energy of dissociation of the $^2\Pi$ state is approx. 15,000 cm^{-1} . A. B. D. CASSIE.
- Nuclear moment of gallium.** D. A. JACKSON (*Z. Physik*, 1932, 75, 229—230).—Both Ga isotopes have nuclear moment $3/2$. A. B. D. CASSIE.
- Nuclear spin of arsenic.** S. TOLANSKY (*Nature*, 1932, 129, 652).—The fine structures now observed in the lines of the As Π spectrum (6400—4300 Å.) involve transitions between $4p5s$ and $4p5p$ electron configurations. The nuclear spin is $3/2$. L. S. THEOBALD.
- Resonance spectrum of selenium vapour.** W. KESSEL (*Bull. Acad. Polonaise*, 1931, A, 196—200).—The resonance series of Se excited by the mercury 4047 Å. line is most intense at about 600°, and that excited by the 4358.5 Å. line at 750°. The wave-lengths are given in tabular form. The lines form two series of doublets with $\Delta\nu=34.7$ and 29 cm^{-1} , respectively. J. W. SMITH.
- Temperature shift of the transmission band of silver.** J. V. PENNINGTON (*Physical Rev.*, 1932, [ii], 39, 953—956).—The shift of the frequency at which max. transmission is found for Ag when the temp. is varied is explained by Kronig's quantum theory of dispersion in metals (cf. A., 1931, 1209). The calc. rate of shift is in fair agreement with experiment. N. M. BLIGH.
- Emission and absorption of radiation by metallic silver.** F. L. MOHLER (*Bur. Stand. J. Res.*, 1932, 8, 357—364; cf. A., 1931, 781; this vol., 4).—The spectrum emitted by Ag bombarded by 100-volt electrons in a high vac. is similar to that emitted from an Ag probe surface by 7-volt electrons in a Cs discharge, being characterised by a high intensity from the visible to 3600 Å., and decreasing to a very low val. beyond 3200 Å. J. W. SMITH.
- Fluorescence of diatomic tellurium vapour excited by the cadmium arc.** J. PIÉRARD and M. MIGEOTTE (*Bull. Acad. roy. Belg.*, 1932, [v], 18, 246—255; cf. this vol., 439).—Observed and calc. vals. of the frequencies, wave-lengths, and term differences of three new series excited by the 4415.68, 4678.15, and 4799.91 Å. arc lines of Cd are tabulated. The series are contrasted with those excited by the Cd spark. N. M. BLIGH.
- Absorption bands of iodine and tellurium.** E. HIRSCHLAFF (*Z. Physik*, 1932, 75, 315—324).—Predissociation was observed in the spectrum of Te_2 at 3895 Å. 50 band edges were measured between 7000 and 9000 Å. in the I_2 spectrum. A. B. D. CASSIE.

Resonance spectra of iodine vapour at high temperatures. E. HIRSCHLAFF (Z. Physik, 1932, 75, 325—337).—A resonance spectrum was observed between 2400 and 4800 Å. on exciting I vapour at 600° with Hg line 2537 Å.; He did not change the bands. A. B. D. CASSIE.

Anti-Stokes terms in the fluorescence spectrum of I_2 . J. J. AGARBICEANU (Compt. rend., 1932, 194, 1338—1340; cf. A., 1922, ii, 177; 1931, 7, 667).—The fluorescence spectrum of I_2 excited by the Hg line 5461 Å. is shown to contain in addition to terms of order (0), (1), (3), and (5), the anti-Stokes terms (-1) and (-2). Hence the quantum no. v'' (=0) cannot be ascribed to the final level of vibration of order (0) ($\lambda=5461$). C. A. SILBERRAD.

Separation of the 2F levels of Ce IV. R. BRUNETTI and Z. OLLANO (Z. Physik, 1932, 75, 415—416).—Raman photographs of conc. solutions of $CeCl_3$ and $Ce(NO_3)_3$ gave the displacements 1640 and 1473 cm^{-1} , respectively, probably due to electronic transitions between the 2F levels of the Ce^{+3} ion. A. B. D. CASSIE.

Transparency of thin platinum sheets in the wave-length range 0.25—2.5 μ . E. SCHUCH (Ann. Physik, 1932, [v], 13, 297—314).—For thinnest sheets there is an increase of transparency with increasing wave-length. There is a thickness at which the effect over a wave-length range of 0.25—1.0 μ is the same. Reflexion determinations in the visible range were carried out. A. J. MEE.

Supposed proof of a nuclear moment for the even isotope of Hg, 198. L. A. SOMMER (Z. Physik, 1932, 75, 134—136).—Polemical, against Schüler (this vol., 4). The isotope 198 has no nuclear moment. A. B. D. CASSIE.

Fluorescent excitation of mercury by the resonance frequency and by lower frequencies. III. (LORD) RAYLEIGH (Proc. Roy. Soc., 1932, A, 135, 617—627).—A method is devised for studying the band spectrum of Hg produced by absorption of the at. resonance line (core excitation) over a range of temp. at one photographic exposure. At 20 mm. pressure the max. 3300 Å. is greatly enhanced by heating, and the wing series bands come into view. At 2 mm. the max. 3300 Å. is diminished by heating. Wood's bands, 2345, 2338, 2334, 2330 Å., come out conspicuously in core excitation. The "forbidden" line 2270 Å. is recorded in fluorescence for the first time. L. L. BIRCUMSHAW.

Hyperfine structure of mercury. K. MURAKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 97—100; cf. this vol., 315).—Using a Geissler discharge and Aron's lamp the structure of the zero lines of $\lambda\lambda$ 5461, 4358, and 4077 was obtained. Intensities and separations of the components of λ 3984 and λ 6123 are tabulated. N. M. BLIGH.

Fluted band at 3900 Å. in the spectrum of mercury. J. OKUBO and E. MATUYAMA (Nature, 1932, 129, 653). L. S. THEOBALD.

Hyperfine structure of the thallium arc lines. D. A. JACKSON (Z. Physik, 1932, 75, 223—228).—

Observed hyperfine structure agrees with two Tl isotopes of nuclear moment 1/2. A. B. D. CASSIE.

Nuclear moment of three lead isotopes. H. KOPFERMANN (Z. Physik, 1932, 75, 363—379).—The Pb isotopes 206 and 208 have probably nuclear moment zero, and 207 has 1/2. A. B. D. CASSIE.

Positive column in diatomic gases. R. HOLM (Z. Physik, 1932, 75, 171—190).—Potential gradients in the positive column of diat. gases agree with Schottky's theory (*ibid.*, 1924, 25, 637), and indicate the presence of negative ions. A. B. D. CASSIE.

Light-intense excitation of spectra in the electric vacuum furnace by electron collisions of small energy. R. RITSCHL (Ann. Physik, 1932, [v], 13, 337—357).—The apparatus is described. The arc spectra of Cu, Au, Be, and Al were investigated. A. J. MEE.

Coupling broadening and collision damping. V. WEISSKOPF (Z. Physik, 1932, 75, 287—301).—Theoretical. A. B. D. CASSIE.

Uniqueness of the decomposition of an intensity curve into its components. E. LONN (Z. Physik, 1932, 75, 348—349). A. B. D. CASSIE.

Excitation of some nebular lines by disruptive discharge. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1932, 8, 78).— H_2 lines of nebular spectra are reproducible in the laboratory, whilst lines of N_2 and O_2 are difficult to obtain. A disruptive discharge method is described. W. R. ANGUS.

Infra-red lines in the spectrum of the aurora. L. VEGARD (Naturwiss., 1932, 20, 268—269).—Neither the anticipated O_2 triplets nor the lines of the second positive group of N_2 have been observed in the near infra-red spectrum of the aurora. The strongest band head corresponds with the $1 \rightarrow 0$ transition of the first positive group of N_2 . J. W. SMITH.

Spectrum of solar corona. T. L. DE BRUIN (Naturwiss., 1932, 20, 269).—New terms have been discovered in the neutral O_2 spectrum enabling several strong lines in the solar spectrum to be interpreted. J. W. SMITH.

Red oxygen radiation in the night sky. L. A. SOMMER (Naturwiss., 1932, 20, 330—331).—A reply to Grotrian (this vol., 441). W. R. ANGUS.

[Red oxygen radiation in the night sky.] W. GROTRIAN (Naturwiss., 1932, 20, 331).—A rejoinder (cf. preceding abstract). W. R. ANGUS.

Spectra of light zones at the cathode of glow discharges. A. GÜNTHER-SCHULZE and F. KELLER (Z. Physik, 1932, 75, 105—110). A. B. D. CASSIE.

Scattering of fast cathode rays in single crystals. F. KIRCHNER (Ann. Physik, 1932, [v], 13, 38—58). W. R. ANGUS.

Atom factors for X-rays in the region of anomalous dispersion. D. COSTER and K. S. KNOL (Z. Physik, 1932, 75, 340—347).—A theoretical discussion indicates that the influence of anomalous dispersion on atom factors, near a K -absorption edge, increases with the angle of reflexion: this agrees with experimental results obtained for Zn crystals. A. B. D. CASSIE.

Continuous and continuous-discrete X-ray spectrum. A. W. MAUE (Ann. Physik, 1932, [v], 13, 161—190).—The retardation of electrons at nuclei gives rise to a continuous and a discrete spectrum. A. J. MEE.

Absolute measurements of X-rays with an electron counter. A. HUPPERTSBERG (Z. Physik, 1932, 75, 231—248).—Electrons ejected from the walls of an electron counter by X-rays may be used as a measure of the intensity of the beam; the counter gave ionisation proportional to the irradiated surface and to the intensity of the beam.

A. B. D. CASSIE.

Dependence of the ratio of intensity of secondary X-ray lines on the wave-length of the exciting radiation. E. ALEXANDER (Z. Physik, 1932, 75, 391—394).—The intensity ratio $Ag L\beta_2 : L\beta_3$ changes from 4 : 1 to 1.33 : 1 when the exciting wave-length is changed from 2.6 to 1.3 Å., and the absorption ratio changes in agreement with Sommerfeld and Schur's theory (A., 1930, 391). A. B. D. CASSIE.

Reflexion and absorption of long-wave X-rays. E. DERSHEM and M. SCHEIN (Z. Physik, 1932, 75, 395—414).—Absorption coeffs. were determined for He, Ne, A, Kr, N₂, O₂, CO₂, and air at the wave-length 44.6 Å. A. B. D. CASSIE.

Fine structure of X-ray absorption edges. II, III. R. DE L. KRONIG (Z. Physik, 1932, 75, 191—210, 468—475; cf. A., 1931, 993).

A. B. D. CASSIE.

Spectrography of X-rays by transmission of non-canalised rays across a curved crystal. (MILE.) Y. CAUCHOIS (Compt. rend., 1932, 194, 1479—1482; cf. this vol., 246). C. A. SILBERRAD.

Intensity ratio of fluorescent X-ray lines. H. R. ROBINSON (Nature, 1932, 129, 618).

L. S. THEOBALD.

Dependence of the X-ray excited K-spectrum of sulphur on chemical combination. A. FAESSLER (Z. Physik, 1932, 75, 424; cf. A., 1931, 670).—Attention is directed to similar work by Lindh (*ibid.*, 1925, 31, 218).

A. B. D. CASSIE.

Appearance of continuous spectra during cathode-ray bombardment. VI. Vapours and gases. W. M. COHN (Z. Physik, 1932, 75, 544—554).—A tube with a Lenard window was used to obtain these continuous spectra outside the discharge tube. The spectrum observed was independent of the window material, was always continuous with a max. at 4500 Å., and in no case extended below 3000 Å.

A. B. D. CASSIE.

Ionisation of argon and neon by neutral argon beams. O. BEECK (Proc. Nat. Acad. Sci., 1932, 18, 311—313).—The production of neutral A atoms is described; a qual. study of intensity of ionisation and atom speed was made, and possible ionisation mechanisms are discussed.

N. M. Blich.

Ionisation in gases by ions and atoms. F. ZWICKY (Proc. Nat. Acad. Sci., 1932, 18, 314—318).—The quant. relations governing ionisation are interpreted, and predictions therefrom relative to ionisation by neutral atoms are discussed (cf. preceding abstract).

N. M. Blich.

Dependence of the photo-emission from potassium on the arrangement of atomic hydrogen and potassium layers on its surface. P. I. LUKIRSKY and S. RIJANOV (Z. Physik, 1932, 75, 249—257).—Experiments showed that two equal quantities of at. H are adsorbed on a K surface; the first forms a monat. layer below a monat. layer of K and increases the photo-emission, whilst the second is above the K and diminishes the emission. A. B. D. CASSIE.

Photo-ionisation probabilities of atomic potassium. (Miss) M. PHILLIPS (Physical Rev., 1932, [ii], 39, 905—912; cf. Lawrence, A., 1929, 1356).—Mathematical. N. M. Blich.

Photo-electric absorption in hydrogen-like atoms. P. A. M. DIRAC and J. W. HARDING (Proc. Camb. Phil. Soc., 1932, 28, 209—218).—Mathematical. N. M. Blich.

Secondary electron emission from nickel and ferromagnetism. P. TARTAKOVSKI and V. KUDR-JAVZEVA (Z. Physik, 1932, 75, 137—142).—At the Curie point secondary electron emission changes discontinuously. The secondary electrons are thus associated with ferromagnetism, and if they are identical with conductivity electrons, ferromagnetism is due to conductivity electrons. A. B. D. CASSIE.

Emission of radiation by the retardation of protons and rapid electrons. O. SCHERZER (Ann. Physik, 1932, [v], 13, 137—160).—Theoretical.

A. J. MEE.

Polarisation of electrons by crystal reflexion. J. THIBAUD, J. J. TROLLAT, and T. VON HIRSCH (Compt. rend., 1932, 194, 1223—1225).—No definite evidence of such polarisation could be found, confirming Thomson's result (cf. A., 1931, 12), but in opposition to that of Rupp (cf. A., 1930, 392).

C. A. SILBERRAD.

Surface electrons. J. E. NYROP (Physical Rev., 1932, [ii], 39, 967—976).—The theory of surface electrons covering the surface of a conductor is applied to the ordinary and selective photo-effect and the evaporation from heated metals. The absorption and catalytic effect of metallic surfaces and the potential barrier which accounts for the work function can be calc. N. M. Blich.

Diffraction of electrons by thin films of paraffin. J. HENGSTENBERG and J. GARRIDO (Anal. Fis. Quim., 1932, 30, 175—181).—Thin films of paraffin (m. p. 40—45°) on collodion, prepared by evaporation of a dil. solution in C₆H₆, have been examined by determination of the electron diffraction diagram. The *c* axes are perpendicular to the plane of the film, and hexagonal orientation is apparent in the *ab* plane. The results indicate that the films consist of thin laminar crystals, and not of crystals having a 3-dimensional lattice. H. F. GILLBE.

Diffraction of electrons in pure and passive iron. W. BOAS and E. RUPP (Ann. Physik, 1932, [v], 13, 1—8).

W. R. ANGUS.

Scattering of slow electrons by neutral atoms. E. FEENBERG (Physical Rev., 1932, [ii], 40, 40—54).—Mathematical. N. M. Blich.

Secondary electron emission from metals. H. FRÖHLICH (Ann. Physik, 1932, [v], 13, 229—248).—Theoretical. For the liberation of secondary electrons there is a lower limit to the primary energy of about 10 volts. The secondary electrons have a velocity below 25 volts, independent of the primary energy.

A. J. MEE.

Free electrons of ionised gases in a magnetic field. T. V. IONESCU and C. MIHUL (Compt. rend., 1932, 194, 1330—1332; cf. this vol., 209).

C. A. SILBERRAD.

Method of observing the scattering of slow electrons. A. BÜHL (Naturwiss., 1932, 20, 317).

W. R. ANGUS.

Collisional friction on electrons moving in gases. E. C. CHILDS (Phil. Mag., 1932, [vii], 13, 873—887).—The frictional coeff. in air is of the same order as the val. calc. from kinetic theory.

H. J. EMELÉUS.

Molecular dissociation by electron impact. F. L. ARNOT (Nature, 1932, 129, 617—618).—Attention is directed to the neglect of radial potential gradients in determining the energies of the dissociation products of N_2 and CO formed by electron impact (cf. this vol., 321).

L. S. THEOBALD.

Photo-dissociation of atomic molecules into ions. A. TEREININ and B. PAPOV (Z. Physik, 1932, 75, 338—339).—The photo-currents observed in TII and TIBr vapours (cf. A., 1930, 1238) were shown by mol. ray methods to be due to dissociation into Ti^+ and (halogen $^-$), and not to the liberation of electrons. If the electron affinities of I and Br be 3.16 and 3.4 volts, the energies of dissociation of TII and TIBr into ions are 5.5 and 5.9 volts.

A. B. D. CASSIE.

Production of high-speed light ions without the use of high voltages. E. O. LAWRENCE and M. S. LIVINGSTON (Physical Rev., 1932, [ii], 40, 19—35).—A method of multiple acceleration of ions to high speeds is described. A current of 10^{-9} amp. of 1,220,000 volt-protons for a max. applied voltage of 4000 has been obtained.

N. M. BLIGH.

Recombination of ions in gases at high pressures. W. R. HARPER (Proc. Camb. Phil. Soc., 1932, 28, 219—233).—Previous theories of the recombination of ions in gases are inapplicable to high pressures; taking into account the effect of thermal agitation and mutual attraction, a theory, in agreement with experimental data, is developed.

N. M. BLIGH.

Conditions of operation of an expansion chamber for H-rays. S. GORODETZKY (J. Chim. phys., 1932, 29, 63—66).—A Wilson expansion chamber provides a convenient method of studying H-rays. The curve relating the range to the frequency of occurrence of the range shows a pronounced min. at about 7.5 cm.

J. W. SMITH.

Observation of neutral H_3 in canal rays. R. CONRAD (Z. Physik, 1932, 75, 504—511).—A method, that reveals whether or not charged particles are neutral over part of their range, showed the existence of H_3 with a half-val. period of 3×10^{-8} sec.

A. B. D. CASSIE.

Charge cross-section of hydrogen mols. in relation to slow protons. N. BARTELS (Ann. Physik, 1932, [v], 13, 373—376).—There is a max. cross-section at about 7 kv.

A. J. MEE.

Report of the Atomic Weight Commission of the International Union for Chemistry. G. P. BAXTER, M. CURIE, O. HÖNIGSCHMID, P. LEBEAU, and R. J. MEYER (Ber., 1932, 65, [A], 33—42).—The report follows the usual lines. The following changes are adopted. Kr 83.7 and X 131.3, instead of 82.9 and 130.2, respectively. In agreement with Aston the Commission considers a change from the accepted bases of chemical at. wts., O=16.0000, to be undesirable.

H. WREN.

At. wt. of fluorine. E. MOLES (J. Chim. phys., 1932, 29, 53—62).—A crit. survey of recent determinations of the at. wt. of F indicates a probable val. of 19.000. There is no experimental evidence for the existence of a heavier isotope of F in any large quantity.

J. W. SMITH.

Distribution of elements in nature, and the atomic volume curve. I. I. ZASLAVSKI (J. Gen. Chem. Russ., 1931, 1, 1080—1082).—The most widely-distributed elements are those at the minima of the at. vol.—at. no. curve.

R. TRUSZKOWSKI.

Hydrogen isotope of mass 2 and its concentration. H. C. UREY, F. G. BRICKWEDDE, and G. M. MURPHY (Physical Rev., 1932, [ii], 40, 1—15).—Samples of H_2 from the last few c.c. of large quantities evaporated at atm. pressure and at a few mm. above the triple point were investigated for the visible at. Balmer series of H^2 and H^3 from a H discharge tube. With a time of exposure increased 4000 times very faint lines at the calc. positions for H^2 appeared as broad doublets. The $H^{2\alpha}$ line was resolved into a close doublet with separation agreeing with that for $H^{2\alpha}$. Estimated relative abundances of H^2 and H^1 in natural H_2 are 1 : 4000, agreeing with that required for an explanation of the discrepancy between the at. wts. of H as determined chemically and by the mass spectrograph.

N. M. BLIGH.

Measurements of the intensity ratio of the neon isotopes, Ne^{20} and Ne^{22} . L. S. ORNSTEIN and J. A. VREESWIJK, jun. (Z. Physik, 1932, 75, 109—110).—This isotope ratio is 10 : 1, giving an at. wt. of 20.18 for atm. Ne.

A. B. D. CASSIE.

Regularities in the structure of isotopes. A. CARRELLI (Z. Physik, 1932, 75, 111—114).—Nuclei of the type $4N_a+1$, $4N_a+2$, and $4N_a+3$ are associated with those of type $4N_a$.

A. B. D. CASSIE.

Copper isotopes. (Miss) E. R. BISHOP (Physical Rev., 1932, [ii], 40, 16—18).—A magneto-optic method shows that Cu has an isotope of at. wt. <63, less abundant than Cu^{63} and Cu^{65} .

N. M. BLIGH.

Isotopic constitution of lead from different sources. F. W. ASTON (Nature, 1932, 129, 649).—Isotopic analyses of Pb from four different sources have been amplified, and several rare isotopes previously suspected in ordinary Pb (A., 1927, 806) have been confirmed. Data for ordinary Pb, Pb from Katanga pitchblende, Wilberforce uraninite, and Norwegian thorite are recorded. The quantities of

Pb²⁰⁶ and Pb²⁰⁷ in the last-named do not correspond with those expected from ordinary Pb as impurity.

L. S. THEOBALD.

Periodical properties of atomic nuclei. G. I. POKROVSKI (Science, 1932, 75, 443—444).—The no. of isotopes having the same at. wt. is a function of this at. wt., and the curve obtained by plotting these nos. against at. wts. resembles the at. vol.—at. wt. curve. The no. of isotopes having the same at. wt. is determined by the properties of the nuclei, the at. vol. by the properties of the electron sheaths of the atom, and since both cases show the same periodicity there must be a connexion between the outer electrons and the protons and electrons in the nucleus.

L. S. THEOBALD.

Mobility of radioactive atoms on the surface of solid bodies. H. JEDRZEJOWSKI (Compt. rend., 1932, 194, 1340—1343).—A patch of Po on Pt foil heated in a quartz tube to 600—637° spreads increasingly over the whole surface of the foil, only about 1/10th being evaporated and found on the quartz. On Au at 1000° there is very little spreading, evaporation predominating, and on mica at 440° almost exclusively evaporation. It is suggested that the Po diffuses along the surface of the Pt (cf. A., 1926, 467; 1929, 737).

C. A. SILBERRAD.

Radioactivity of potassium. P. AUGER (Compt. rend., 1932, 194, 1346—1347; cf. Perrin, this vol., 556).—Assuming K⁴¹ to consist of 10 helions, 1 neutron, and 1 electron, the emission of the neutron and electron would leave ordinary Ca⁴⁰, thus explaining the absence of the isotope Ca⁴¹ (cf. A., 1928, 1169). A similar explanation applies to Rb and Sr.

C. A. SILBERRAD.

Half-value period of uranium-X₁. E. WALLING (Z. Physik, 1932, 75, 432—433).—The half-val. period of U-X₁ is 24.5 days.

A. B. D. CASSIE.

Fine structure of α -radiation of radiothorium. S. ROSENBLUM and (MLLE.) C. CHAMÉ (Compt. rend., 1932, 194, 1154—1155; cf. A., 1931, 280).—The α -magnetic spectrum of Rd-Th (prepared from BaCl₂ containing Ms-Th) contains (figures denote velocities in cm. $\times 10^{-9}$ /sec.) Rd-Th α_1 1.612(4), strong; Rd-Th α_2 1.600(3), medium; and a very weak ray α_x 1.594(2) of uncertain origin; and (from an older prep.) Th-A 1.802(3); Th 1.736(0), and Th-X 1.650(8).

C. A. SILBERRAD.

Fluctuations of the rate of emission of α -particles for weak sources and large solid angles. L. F. CURTISS (Bur. Stand. J. Res., 1932, 8, 339—346).

Penetrating radiation excited in light nuclei by α -particles. (MME.) I. CURIE and F. JOLIOT (Compt. rend., 1932, 194, 1229—1232).—From a consideration of the absorption of the radiation from Po+Be (cf. this vol., 318) in Pb, and the dissymmetry of the radiation emission as a function of the thickness of Pb interposed between the source and the ionisation chamber (containing successively A, N₂, and He), it is concluded that Be thus irradiated emits a complex radiation in which are recognisable (1) a γ -radiation absorbed by a Compton effect on the electrons, emitted approx. equally in all directions, and of energy up to 4×10^6 electron-volts; and (2) a very penetrating radiation absorbed by projection of nuclei,

and emitted dissymmetrically relatively to the direction of the incident α -particles. C. A. SILBERRAD.

Fine structure of α -magnetic spectrum of radioactinium. (MME.) P. CURIE and S. ROSENBLUM (Compt. rend., 1932, 194, 1232—1235).—The α -magnetic spectrum of Rd-Ac, prepared by Curie's method (cf. A., 1931, 783), contains (figures indicate velocities in 10^{-9} cm./sec.): α_1 1.703, strong; α_2 1.700, feeble; α_3 1.695, very strong; ? (1.683), feeble; α_4 1.676, feeble; α_5 1.662, strong; and α_6 1.656, very strong. Energy differences correspond to a certain extent with the γ -rays due to Rd-Ac (cf. A., 1926, 105). Other rays found as the preps. aged were: Ac-A 1.883; Au 1.810; Ac-C α 1.783; Ac-C α_1 1.734; Ac-X α_1 1.640, strong; and Ac-X α_2 1.631, feeble.

C. A. SILBERRAD.

Decrease in velocity of α -particles from thorium-C' in air. G. MANO (Compt. rend., 1932, 194, 1235—1237).—If v_0 is the initial velocity of an α -particle and v its velocity after passing through p cm. of air, the deviation from Geiger's law is expressed by $\epsilon = v/v_0 - (1 - p/\pi)^{1/3}$, where $\pi = 8.54$ cm., the mean free path of the α -particles. Results agree with other determinations (cf. A., 1931, 1349; this vol., 442).

C. A. SILBERRAD.

Artificial disintegration of certain elements by the α -rays of polonium. M. C. PAVLOVSKI (J. Phys. Radium, 1932, [vii], 3, 116—126).—The disintegration of elements by bombardment with the α -rays of Po has been studied by determining the no. of particles emitted in a direction making an angle of 130° with the direction of the incident radiation. H-Radiation has been obtained in the case of C, Mg, Al, Si, and S, confirming the results of other investigators that it is possible to disintegrate elements of an at. wt. which is a multiple of 4. The extent of disintegration obtained agrees most closely with that observed by Bothe and Fränz (A., 1928, 810). No disintegration was obtained in the case of Fe, Zn, Ag, and Pb.

M. S. BURR.

Permanent magnet for β -ray spectroscopy. J. D. COCKCROFT, C. D. ELLIS, and H. KERSHAW (Proc. Roy. Soc., 1932, A, 135, 628—636).—The construction and use of a large permanent magnet, by means of which a max. field of 2300 gauss is obtainable, are described.

L. L. BIRCUMSHAW.

Diffusion of β -radiation by the support carrying the radioactive material. Importance of this effect in determination of these materials. (MLLE.) A. POMPEI (J. Chim. phys., 1932, 29, 77—80).—The intensity of the β -radiation from a radioactive deposit increases with the at. wt. of the supporting material, a Pb support leading to 50% greater intensity than an Al support. This should be taken into account when determining radioactive materials by their β -radiation.

J. W. SMITH.

β - and γ -radiation of uranium-Z. The branching ratio of uranium-Z to the principal branch of the uranium series. E. WALLING (Z. Physik, 1932, 75, 425—431).—Studies of the absorption of radiation emitted by U-Z showed these to consist of two penetrating β -rays and a penetrating γ -ray. 3% of U-X₁ disintegrates into U-Z. A. B. D. CASSIE.

Absolute energies of the lines in β -ray spectra. C. D. ELLIS (*Nature*, 1932, 129, 691).—Published vals. of the energies of the lines in the Th-B+C and in the Ra-B+C spectra may be high. L. S. THEOBALD.

Spectrum of γ -rays from derivatives of radiothorium. D. SKOBELZYN (*Compt. rend.*, 1932, 194, 1486—1488; cf. A., 1927, 710; 1930, 8).—Using the method described previously, the γ -spectrum of Ra-Th (rays filtered through 30 mm. of Pb, angle of emission $>10^\circ$) has been examined and the energy of the secondary Compton electrons determined. In addition to the chief max. for 2650 kv. (due to Th-C''), smaller max. occur for 2000 and 1650 kv. Ms-Th+Ra-Th shows a similar distribution with a still smaller max. for about 1550 kv. C. A. SILBERRAD.

Homogeneity of filtered γ -rays of thorium-C'' and the verification of the Klein-Nishina formula. D. SKOBELZYN (*Compt. rend.*, 1932, 194, 1568—1571; cf. preceding abstract).—The bearing of the softer rays found by the author on the verification of the Klein-Nishina formula as regards γ -rays from Th-C'' (cf. A., 1931, 142, 281, 995) is discussed. σ_r (for Al) and the effective wave-lengths (in X.) of the principal ray and of rays after filtration through 3 and 4 cm. of Pb, respectively, are 0.098, 4.7; 0.105, 5.3; and 0.103, 5.1, correct to ± 0.001 . C. A. SILBERRAD.

Penetrating beryllium radiation. F. RASETTI (*Naturwiss.*, 1932, 20, 252—253; cf. this vol., 443).—The behaviour of Be radiation, produced by the action of α -rays from Po on Be, suggests that it is a mixture of neutrons and γ -rays. Using an ionisation chamber, the data obtained are primarily due to the neutrons, and substances containing H appear to absorb the radiation abnormally, whereas with a counter γ -rays are detected and the absorption of paraffin etc. appears to be normal. J. W. SMITH.

Existence of neutrons and constitution of light atomic nuclei. F. PERRIN (*Compt. rend.*, 1932, 194, 1343—1346).—The possibility of the very penetrating radiation emitted by Be under the influence of Po (cf. this vol., 555) consisting of neutrons is deduced from Fournier's theories (cf. A., 1930, 269), which are extended to suggest constitutions for several elements of helions (α -particles), protons, and neutrons, and also the radiation emitted or emissible by each. C. A. SILBERRAD.

Constitution of atomic nuclei. G. FOURNIER (*Compt. rend.*, 1932, 194, 1482—1483; cf. A., 1930, 1087, and preceding abstract).—Theoretical. Atoms are built up of neutrons, demi-helions (consisting of two protons and one electron—the nucleus of H²), and helions, and disintegrate by loss of a helion, demi-helion, neutron, or an electron. C. A. SILBERRAD.

Passage of neutrons through matter: a correction. H. S. W. MASSEY (*Nature*, 1932, 129, 691; cf. this vol., 443). L. S. THEOBALD.

Disintegration of lithium by swift protons. J. D. COCKROFT and E. T. S. WALTON (*Nature*, 1932, 129, 649).—Bombardment of Li by protons moving under an accelerating potential of 125 kv. produces scintillations which increase rapidly with an increase in voltage up to 400 kv. The range of the particles

is approx. 8 cm. in air and does not vary greatly with voltage. The brightness of the scintillations and the density of the tracks observed in an expansion chamber indicate that the particles are normal α -particles; at 250 kv., 1 particle per 10^9 protons is estimated to be produced. Li⁷ may occasionally capture a proton and the resulting nucleus of mass 8 may break into 2 α -particles, mass 4, and each with an energy of approx. 8×10^6 electron volts. L. S. THEOBALD.

Ionisation by penetrating radiation as a function of pressure and temperature. A. H. COMPTON, R. D. BENNETT, and J. C. STEARNS (*Physical Rev.*, 1932, [ii], 39, 873—882).—The approach to a limiting val. at high pressures of the ionisation of a gas by γ - or cosmic rays is explained by ionic reunion. Relations between saturation ionisation current and pressure are obtained. N. M. BLIGH.

Disintegration of lead by cosmic radiation. E. G. STEINKE and H. SCHINDLER (*Z. Physik*, 1932, 75, 115—118).—Cosmic radiation apparently ejects H nuclei, with a range of 10 cm. in Pb, from the Pb shields of ionisation chambers; the frequency of this ejection disagrees with the hypothesis that cosmic radiation consists of electrons. A. B. D. CASSE.

Cosmic-ray particles. G. L. LOCHER (*Physical Rev.*, 1932, [ii], 39, 883—888; cf. this vol., 5).—Sp. ionisation along the tracks previously found has been determined. Explanations of group phenomena in the tracks are discussed. N. M. BLIGH.

Tables of the ionisation in the upper atmosphere. E. O. HULBURT (*Physical Rev.*, 1932, [ii], 39, 977—992; cf. A., 1930, 392). N. M. BLIGH.

Hydrogen nucleus of mass 2 (isohydrogen nucleus p_2e) as a unit in atom building. W. D. HARKINS (*J. Amer. Chem. Soc.*, 1932, 54, 1254—1256). C. J. WEST.

Structure of atomic nuclei. C. D. ELLIS (*Nature*, 1932, 129, 674—676).—A report of a discussion of the recent work (cf. this vol., 443). L. S. THEOBALD.

Pauli's principle and the structure of the atomic nucleus. II. E. N. GAPON (*J. Gen. Chem. Russ.*, 1931, 1, 1089—1094).—The at. wt. of isotopes of elements of the H—Cu series can be derived from Aston's and Pauli's principles, and from the principle of increasing complexity of the nucleus. R. TRUSZKOWSKI.

Electronic radius. M. BORN (*Naturwiss.*, 1932, 20, 269).—It is suggested that the electronic radius should be defined as the effective radius with respect to photon collision, in which case it is expressed by $r = \frac{1}{3} \sqrt{8 \times e^2 / m_0 c^2}$. J. W. SMITH.

Calculation of the atomic constants, e , h , and N , from Rydberg number, specific electronic charge, and measurement of short-wave limit of the Röntgen spectrum. F. KIRCHNER (*Ann. Physik*, 1932, [v], 13, 59—62).—Using the measurements of the short-wave limit of the Röntgen spectrum of Duane (I) and of Feder (II) together with the val. for $h/e^{5/3}$ ($= 2.2494 \times 10^{-11}$) obtained from the Rydberg formula, the following vals. are obtained: from (I) $e = 4.798 \pm 0.006 \times 10^{-10}$, $h = 6.615 \pm 0.012 \times 10^{-27}$, $N = 6.029 \pm 0.008 \times 10^{23}$; and from (II) $e = 4.782 \pm 0.006 \times$

10^{-10} , $h = 6.577 \pm 0.012 \times 10^{-27}$, $N = 6.049 \pm 0.008 \times 10^{23}$. The vals. of the reciprocal of the fine structure const. are (I) 137.09 and (II) 137.25. W. R. ANGUS.

Mass of the electron. W. DUANE (Proc. Nat. Acad. Sci., 1932, 18, 319—322).—From the val. of m_0 calc. from experimental data, without using vals. of e and h , vals. of these const. from available measurements of e/m_0 by various methods are compared. N. M. BLIGH.

Precision measurements of the crystal parameters of some of the elements. E. A. OWEN and J. IBALL (Phil. Mag., 1932, [vii], 13, 1020—1028).—Parameters of the following elements, showing cubic symmetry, were measured: Ag 4.0773, Al 4.0406, Cu 3.6076 Å. (all ± 0.0003 Å.); Au 4.071, Ir 3.831, Mo 3.140, Ni 3.517, Pb 4.939, Pd 3.885, Rh 3.795, Ta 3.311, W 3.159 Å. (all ± 0.001 Å.).

H. J. EMELÉUS.

Natural colours of various glasses and colours produced by radiation and fluorescence. J. HOFFMANN (Z. anorg. Chem., 1932, 205, 193—204; cf. A., 1931, 579).—Very small proportions of alkali sulphate change the brown radiation colour due to Na atoms into greenish-yellow. The coloration of 12 glasses containing Mn and Mn with Fe by ultra-violet light and by β - and γ -rays has been examined. It is considered that violet radiation colours are due to Mn^{+++} and Mn^{++} ions, and blue to manganomanganic ions. The colour of amethyst is not due to alkali-metal atoms. F. L. USHER.

Action of a transverse electrostatic field on flames. J. K. MCNEELY and E. W. SCHILLING (Iowa State Coll. J. Sci., 1931, 6, 1—9).

CHEMICAL ABSTRACTS.

Interpretation of spectrograms. A. H. TAYLOR and T. KNOWLES (J. Opt. Soc. Amer., 1932, 22, 229—235).—The use of diffusing quartz over the slit of the spectrograph is recommended to secure even illumination. Other precautions in the making and interpretation of spectrograms are detailed.

J. LEWKOWITSCH.

Line reflexion spectra of solids. F. H. SPEDDING and R. S. BEAR (Physical Rev., 1932, [ii], 39, 948—952).—A new interpretation of reflexion spectra in solids, particularly $SmCl_3 \cdot 6H_2O$, is proposed. The difference in spectrum of a conglomerate compared with that of a single crystal is attributed to increased path length through the crystal rather than to surface atoms. A new phenomenon of reversal of lines from absorption in a single crystal to emission in a conglomerate is described for a multiplet of the $GdCl_3 \cdot 6H_2O$ spectrum (cf. A., 1929, 1362).

N. M. BLIGH.

Light from solidified gases. Relations between electronic levels and phosphorescence of gaseous nitrogen. L. VEGARD (Z. Physik, 1932, 75, 30—62).—By means of a new phosphoscope the phosphorescent radiation emitted by solid N_2 and NO under bombardment of cathode rays of up to 6000 volts was analysed as far as 1600 Å. Positive and negative N_2 bands were not observed, showing them peculiar to the gaseous phase; NO with 1% of A gave N_2 bands. The ϵ -system was analysed, and its end level has an energy of dissociation of 11.5

volts. A new scheme for the A, B, C, and D electronic levels leads to possible new explanations of active N_2 . A. B. D. CASSIE.

Emission and absorption spectra of BaF. F. A. JENKINS and A. HARVEY (Physical Rev., 1932, [ii], 39, 922—931).—Electronic terms and vibration frequencies are tabulated for BaF, LaO, SrF, YO, CaF, and ScO and classified for BaF. Existing data are revised and corrected. N. M. BLIGH.

Absorption of water in the visible spectral region. B. LANGE and C. SCHUSTERIUS (Z. physikal. Chem., 1932, 159, 303—305).—Determination of the absorption coeff. between 400 and 800 $m\mu$ by a photoelectric method has revealed absorption maxima at 600, 660, and 750 $m\mu$. The absorption of the shorter wave-lengths is quite small, but is considerably increased by the presence of impurities.

R. CUTHILL.

Absorption of light by aqueous potassium permanganate solutions. B. LANGE and C. SCHUSTERIUS (Z. physikal. Chem., 1932, 159, 295—302).—Determination of the absorption curve of 0.01N- $KMnO_4$ by means of unidirectional photo-cells has shown that between 450 and 700 $m\mu$ there are absorption maxima at 490, 508.4, 526.5, 546.5, and 566 $m\mu$ only. On dilution to $10^{-5}M$ the bands are not displaced; Beer's law holds. R. CUTHILL.

Absorption spectra of the rare earths. II. Y. UZUMASA (Bull. Chem. Soc. Japan., 1932, 7, 85—91).—The spectra of $NdCl_3$ and $Nd(NO_3)_3$ in H_2O , glycerol, MeOH, EtOH, and $COMe_2$ have been compared. The effect of Et_2O , C_6H_6 , CCl_4 , and $CHCl_3$ on the spectrum of $Nd(NO_3)_3$ in EtOH has been examined. The position of the Nd bands varies slightly according to the concn., anion, and solvent, displacement being due to deformation of the electron shell of the Nd^{+++} ion by the anion and by solvation. D. R. DUNCAN.

New band system of beryllium oxide. L. HERZBERG (Nature, 1932, 129, 653—654).

L. S. THEOBALD.

Chromium oxide and vanadium oxide band spectra. W. F. C. FERGUSON (Bur. Stand. J. Res., 1932, 8, 381—384).—Measurements have been made of the band heads due to CrO and to VO, and vibrational analyses made of these spectra.

J. W. SMITH.

Relations between the structure of organic molecules and their absorption spectra in the ultra-violet. (MME.) P. RAMART-LUCAS (Bull. Soc. chim., 1932, [iv], 51, 289—338).—A lecture.

Structure and ultra-violet absorption of organic molecules. (MME.) RAMART-LUCAS and J. HOCH (Ann. Chim., 1932, [x], 17, 207—253).—The ultra-violet absorption of the members of the homologous series $Ph[CH_2]_nR$, where R is CO_2H , CO_2Et , CN, $CO \cdot NH_2$, $CH(CO_2H)_2$, or Ph, shows that when n is 1 the chromophores Ph and R may have a marked influence on one another. This influence practically disappears for $n=3$ and the ultra-violet absorption spectrum of the mol. is then practically the same as for a mixture of PhEt and MeR. When the chromophores are separated by 5C the reciprocal influence again becomes manifest, indicating proximity

in space and hence a curvature of the mol. chain. If the chain is sufficiently long, *i.e.*, when n is 6 for acids and 4 for hydrocarbons, the absorption spectrum of the mol. in EtOH solution becomes the same as that of a mixture of PhEt and MeR in C_6H_{14} , but not in EtOH. The result is as if the mol. chain curved around the chromophores and thus prevented the action of the solvent EtOH.

M. S. BURR.

Autoxidation. IV. Absorption spectrum of aqueous solutions of sulphurous acid in relation to their autoxidation. H. W. ALBU and P. GOLD-FINGER (Z. physikal. Chem., 1932, B, 16, 338—350; cf. A., 1931, 1252).—The absorption of the solutions between 1950 and 5000 Å. depends only on the p_H and concn., and, provided that autoxidation is prevented, not on the age or mode of prep. The spectrum of SO_3'' , which is structureless and regarded as an electron affinity spectrum, is observed with solutions of $p_H \geq 6$ and has the long-wave limit of 2660 Å., whilst the absorption of undissociated dissolved SO_2 ($p_H \leq 4$) starts at 3270 and has a max. at 2800 Å. Franck and Haber's theory (*ibid.*, 917) indicates that an electron affinity spectrum of HSO_3' will be 1.5—2 volts nearer the ultra-violet than that of SO_3'' , and in agreement with this there is no evidence of absorption by HSO_3' at wave-lengths > 2250 Å. The long-wave limits of the absorption of S_2O_8'' and S_2O_6'' are 2700 and 2600 Å., respectively. No absorption by SO_4'' was detected.

R. CUTHILL.

Absorption spectrum of cyanogen gas in the ultra-violet. S. C. WOO and R. M. BADGER (Physical Rev., 1932, [ii], 39, 932—937).—Data for more than 100 bands in the region λ 2300—1820, with probable origin at $44,900\text{ cm.}^{-1}$, are tabulated, and relations with the infra-red absorption and Raman spectra are discussed.

N. M. BLIGH.

Predissociation of the benzene molecule in the electronic ground state. F. ALMASY (Naturwiss., 1932, 20, 296—297).—The monochromatically excited fluorescence spectrum of C_6H_6 vapour at pressures < 2 mm. has been examined with large dispersion and the results are discussed.

W. R. ANGUS.

Spectrographic study of some heterocyclic compounds. M. MILONE (Gazzetta, 1932, 62, 154—158).—A study of the absorption spectra of various compounds of the furazan, azoxime, and oxadiazole types shows that the selective absorption depends more on the nature of the side-chain than on the position of the atoms in the C_2N_2O ring.

O. J. WALKER.

Lignin. V. R. O. HERZOG and A. HILLMER (Papier-Fabr., 1932, 30, 205—209; cf. A., 1931, 942).—In the spectrographic examination of phenolic and other substances related to the primary components of lignin it is found that the introduction of phenolic OH groups into the C_6H_6 nucleus causes intensification of the absorption and displacement of the absorption bands towards the region of longer wave-length. The presence of a saturated side-chain, or one containing a double linking in the $\beta\gamma$ position or a carbonyl or OH group in the β position causes no important change in the spectrum. On the other hand, a conjugated double linking in the $\alpha\beta$ position, or a carbonyl group

in the α position, alters the spectrum. The members of a homologous series in which the repeating groups of atoms have a characteristic spectrum show one and the same spectrum. The spectrum of a mixture of substances that do not react with one another is additive.

B. P. RIDGE.

Influence of substitution on the natural frequencies of organic compounds. G. ALLARD (Compt. rend., 1932, 194, 1495—1498).—If ν , $\nu + \delta\nu$, and ν_0 are respectively the frequencies of absorption bands of mols. AB and AC and the group A, $h\delta\nu$ should equal the difference between the energies of perturbation of group A by B and by C (cf. A., 1931, 978, this vol., 7).

C. A. SILBERRAD.

Rotation-vibration bands of water vapour between 0.9 and 6.5 μ . P. LUEG and K. HEDFELD (Z. Physik, 1932, 75, 512—520).—The bands at 9050, 9400, and 11,300 Å. were photographed under high dispersion, and an analysis of the bands up to 6.5 μ gives the moments of inertia as 6.70, 2.13, and 0.97×10^{-40} g. cm.^2

A. B. D. CASSIE.

Parallel type absorption bands of ammonia. D. M. DENNISON and J. D. HARDY (Physical Rev., 1932, [ii], 39, 938—947).—The predicted doubling of the 3.0 μ band is confirmed experimentally. Calc. intensities of the 3.0 and 10.5 μ bands are in good agreement with experiment.

N. M. BLIGH.

Infra-red absorption spectra of the oxides of chlorine. C. R. BAILEY and A. B. D. CASSIE (Nature, 1932, 129, 652—653).—Details are given for Cl_2O and ClO_2 . A determination of mol. const. makes it probable that both SO_2 and ClO_2 are equilateral triangles with sides 1.37 Å. in length, with a single linking between each O and the central atom. The mol. of Cl_2O is triangular with a vertical angle of approx. 90° and with single linkings between the Cl and O atoms. There is a large repulsive force between the two Cl atoms, since the force const. for the particles at the base of the triangle increases from 1.7×10^5 dynes per cm. for SO_2 and ClO_2 to 5×10^5 dynes per cm. for Cl_2O .

L. S. THEOBALD.

Absorption by formaldehyde vapour in the infra-red. J. R. PATTY and H. H. NIELSEN (Physical Rev., 1932, [ii], 39, 957—966).—Bands at 3.5, 1.8, 1.4, 1.25, and a new band at 4.8 μ were observed. The region of intense absorption at 3.5 μ consisted of three partly overlapping bands with centres near 3.4, 3.5, and 3.6 μ . The 4.8 μ band, resolved under high dispersion, showed similar structure.

N. M. BLIGH.

Infra-red spectra and structure of tautomeric compounds. C. E. H. BAWN (J.C.S., 1932, 1189—1198).—The infra-red spectra of acetyl- and benzoyl-acetone, Et acetoacetate and methylacetoacetate have been investigated between 2.8 and 6.3 μ . The spectra show no band characteristic of an O-H linking, as would have been expected for enolised tautomers. The absorption spectra of acids do not show O-H bands, although the C=O bands are found. The absence of bands due to O-H linkings may be due either to no O-H group in the enolic tautomeride or to a displacement of the characteristic band due to the influence of the neighbouring $\cdot C \cdot C \cdot$ group or to

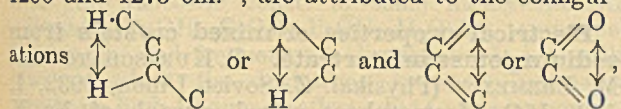
an abnormal vibration of the H atom in the OH group. W. R. ANGUS.

Infra-red absorption spectra of ethylenic and aromatic derivatives. R. FREYMAN (Compt. rend., 1932, 194, 1471—1474; cf. this vol., 6).—The absorption spectra between 0.84 and 1.16 μ of 10 ethylenic and 27 aromatic liquids have been determined: OH, NH₂, CH not attached to C by double linking, CH thus attached, and C:C are characterised respectively by bands at 0.96, 1.03, 0.9 and 1.0, 0.87, and 1.14, and (probably) 1.10 and 1.12 μ . Results indicate identity of effect of double linkings in ethylenic and aromatic compounds. In the latter an electronegative group is accompanied by a shift towards shorter wave-length, a positive group the reverse. C. A. SILBERRAD.

Molecular light scattering by solids. V. Theory of light scattering. M. LEONTOVITSCH and S. MANDELSTAM, jun. (Z. Physik, 1932, 75, 350—351).—A formula is deduced for the intensity of light scattered by rock-salt and other isotropic solids. A. B. D. CASSIE.

Raman effect. G. ELSÉN (Chem. Weekblad, 1932, 29, 183—188, 194—200).—A review of the theory and of some of the more important results which have been obtained. H. F. GILLBE.

Interpretation of certain Raman frequencies of the carbon double linking. G. ELSÉN (Ber., 1932, 65, [B], 525—534).—The Raman lines, ν = about 1200 and 1275 cm.⁻¹, are attributed to the configurations



respectively, present in a variety of aliphatic and aromatic substances. The frequencies are probably simple vibrations, although the possibility of rotations in which valency electrons can participate is not excluded. The theoretical consequences are discussed at length. H. WREN.

Light absorption, the Raman effect, and the motions of electrons in gases. V. A. BAILEY (Phil. Mag., 1932, [vii], 13, 993—1000).—The relation between the energy transferred from a slow electron to a mol. and the energy transferred from radiation to a mol. during absorption or scattering is discussed. H. J. EMELÉUS.

Raman spectrum of water. H. HULUBEI (Compt. rend., 1932, 194, 1474—1477).—The Raman spectrum of H₂O, using the line 2536.52 Å. (cf. A., 1931, 892), shows a double band with max. at 3233 and 3443 cm.⁻¹, but with no trace of a third band (cf. A., 1930, 662); ten other bands (6747—10,944) were also measured, most of which disappear on adding a salt. C. A. SILBERRAD.

Raman effect of salt solutions. A. SILVEIRA (Compt. rend., 1932, 194, 1336—1338).—Using Hg light filtered through quinine sulphate and solutions of MgCl₂, Mg(NO₃)₂, and Mg(ClO₄)₂ about 5.5M, optically purified by ultra-filtration, the Raman spectra include lines at 1652 and 1655 cm.⁻¹ in the chloride and nitrate, respectively, and 376 (feeble) in both, but in the chlorate only doubtfully at 376. It

is inferred that these are due to hydrated Mg⁺⁺ ions, and that the structure of the chlorate solution is essentially different. C. A. SILBERRAD.

Valency- and deformation-oscillations of simple molecules. I. General theory. II. Triatomic molecules. R. MECKE (Z. physikal. Chem., 1932, B, 16, 409—420, 421—437).—I. The theory of the subdivision of the characteristic frequencies of a polyat. mol. into valency- and deformation-oscillations (cf. A., 1930, 1236) is described.

II. Interpretation of the Raman and infra-red spectra of triat. mols. by means of the theory shows that the three atoms lie in the one straight line only if, as in CO₂, CS₂, N₂O, and HCN, a triple linking is present. In such mols. the mutual interaction of the linkings is only 3—6% of the strength of the linking, so that the deformation oscillation is small. With non-linear mols., such as H₂O, H₂S, -CH₂, SO₂, -NO₂, -CCl₂, -CBr₂, and -Cl₂, the mutual interaction is about 30%, and results in stable valency flexure. R. CUTHILL.

Raman spectra of mono-, di-, and tri-saccharides. W. KUTZNER (Naturwiss., 1932, 20, 331—332).—Aldoses are characterised by a Raman displacement of 1140 cm.⁻¹; ketoses by a displacement of 1180 cm.⁻¹. Glucose gives two other displacements of 513 and 454 cm.⁻¹. Maltose shows only the characteristic aldose displacement, whereas sucrose gives a broad band (1130—1188 cm.⁻¹) embracing the characteristic displacements of an aldose and a ketose. The spectrum of raffinose, 1150 cm.⁻¹, is diffuse and weaker than the spectra of other sugars. W. R. ANGUS.

Raman spectra of cyclanes. E. CANALS, M. GODCHOT, and (MLLE.) G. CAUQUIL (Compt. rend., 1932, 194, 1574—1577).—Raman spectra of cyclopropane, -pentane, -hexane, -heptane, and -octane and their Me derivatives show great similarity; lines characteristic of C-H, e.g., that near 800 cm.⁻¹, decline in frequency as the ring enlarges; 1440, characteristic of -CH₂, is almost const.; introduction of Me causes a general lowering of frequency, less as the ring enlarges. Comparison with the corresponding paraffins shows that a line near 1200 characterises the cyclanes (cf. this vol., 109, 213). C. A. SILBERRAD.

Raman spectrum and constitution of substances of high mol. wt. R. SIGNER and J. WEILER (Helv. Chim. Acta, 1932, 15, 649—657).—The Raman spectra of styrene, PhEt, and polystyrene (in the solid state and in CCl₄) are closely similar, but styrene alone shows the lines associated with the ethylenic linking. The results strongly support Staudinger's structure for polystyrene (A., 1929, 305). The continuous background is attributed to fluorescence, due to impurities, or to the end-groups of the polystyrene chain. Venkateswaran's explanation (A., 1928, 1170) is rejected. D. R. DUNCAN.

Luminescent compounds. II. A. SCHLOEMER (J. pr. Chem., 1932, [ii], 133, 257—258; cf. this vol., 352).—ThO₂, moistened with CeO₂ (best 0.9%), dried, and strongly heated, is luminescent in a conc. stream of cathode rays (70 kv.). Luminescence reaches a

max. after 0.5 sec. and rapidly fades on cessation of the excitation.

R. S. CAHN.

Phosphorescent sulphides: intervention of collisions of the second kind. M. CURIE (Compt. rend., 1932, 194, 1566—1568).—The *d*-process absorption bands are due to absorption by mols. of diluent near a light-forming centre, bringing them into an excited state, followed by collisions of the second kind with electrons previously detached from such centre. Such collisions remove the electrons from the influence of the centre and so prolong the fluorescence. Similar collisions explain the max. of *d*-process phosphorescence for certain wave-lengths (cf. A., 1910, ii, 369; 1931, 894).

C. A. SILBERRAD.

Analysis of ultra-violet emission of alkaline-earth phosphors. O. SCHELLENBERG (Ann. Physik, 1932, [v], 13, 249—264).

A. J. MEE.

Electrolytic valve action. A. GÜNTHER-SCHULZE (Z. Physik, 1932, 75, 143).—Polemical against Müller (this vol., 214).

A. B. D. CASSIE.

Nature of the unidirectional layer in cuprous oxide rectifiers. F. WAIBEL and W. SCHOTTKY (Naturwiss., 1932, 20, 297—298).

W. R. ANGUS.

Structure experiments with the cuprous oxide rectifier. K. SCHARF and O. WEINBAUM (Physikal. Z., 1932, 33, 336—341).—A microscopical investigation of the cryst. structure of a Cu_2O rectifier has been made.

A. J. MEE.

Constitution of the oxide of copper oxide rectifiers and of cuprous oxide photo-electric cells. L. DUBAR (Compt. rend., 1932, 194, 1332—1334; cf. A., 1931, 409).— Cu_2O is probably a perfect insulator. The substance causing conductivity in "semi-conducting Cu oxide" is present in very small amount, $> 1.5\%$, disseminated in intercryst. spaces of Cu_2O ; it is possibly CuO in solid or colloidal solution.

C. A. SILBERRAD.

Internal photo-effect and photo-electric cells. I. I. V. KURTSCHATOV and C. D. SINELNIKOV. II. I. KURTSCHATOV, C. SINELNIKOV, and M. BORISSOV (Physikal. Z. Soviet Union, 1932, 1, 23—41, 42—59).—I. The spectral sensitivity, influence of temp. and of electrode material have been investigated for cells with Cu_2O and Cu_2S between metal electrodes. The origin of the e.m.f. is discussed.

II. Results similar to those for Cu_2O were obtained with Se in the cell.

H. J. EMELÉUS.

Catalysis and photo-conductors. [Selenium.] F. H. CONSTABLE and A. F. H. WARD (Trans. Faraday Soc., 1932, 28, 497—508).—Small quantities of Ag, Bi, Pb, Hg, Zn, Cu, and Fe were incorporated in amorphous red Se and thin films of the mixture were annealed at temp. between 170° and 215° . Phase data are given. The effects of illumination are characterised by the light ratios, *L* (current in light/current in dark, at const. applied p.d.) obtained from data at various stages during illumination and subsequent darkness. The "dark resistance," *R*, and vals. of *L* are diminished by Fe, only slightly affected by Zn and Pb, but are increased by Bi, Cu, Hg, Ag, and especially by Tl, at the same annealing temp.

Vals. of *L* are higher at the lower annealing temp. for Se alone and with the added metals. In general, the addition of the metals does not increase median vals. of *L*, for a given resistance, to a higher val. than would correspond with that of a film of pure Se with the same val. of *R*, but distortion of the annealing temp.—*L* curve may occur. The metals, therefore, have little effect on the liberation of electrons by light, but greatly influence the chemical constitution of the cryst. mass.

J. G. A. GRIFFITHS.

Spectral distribution of the depolarisation current due to the photo-electric conductivity of X-rayed rock-salt. N. KALABUCHOV and B. FISCHLEEV (Z. Physik, 1932, 75, 282—286).

A. B. D. CASSIE.

Anomalous variation of the electrical conductivity of quartz with temperature. S. SHIMIZU (Phil. Mag., 1932, [vii], 13, 907—934).—The conductivity increases linearly with rise of temp. up to the transition point at 573° , where a discontinuity occurs. At higher temp. the temp. coeff. is greater, and the conductivity increases with the measuring potential.

H. J. EMELÉUS.

[Two different liquid states.] L. MEYER (Z. Physik, 1932, 75, 421—423).—The hypothesis of two mol. forms (Wolfke and Mazur, this vol., 329) is probably incorrect: the observed change in dielectric const. with temp. is more probably associated with some phenomenon analogous to change from vibration to rotation within the liquid.

A. B. D. CASSIE.

Electrical properties of mixed crystals from sodium potassium tartrate. B. KURTSCHATOV and M. EREMEJEV (Physikal. Z. Soviet Union, 1932, 1, 140—154).—Isomorphous mixed crystals of Na K tartrate and K NH_4 tartrate give anomalous high vals. of the dielectric const. from -107° to -190° . In this range they resemble ferro-magnetic substances.

H. J. EMELÉUS.

Dielectric constants of some oxides. A. GÜNTHER-SCHULZE and F. KELLER (Z. Physik, 1932, 75, 78—83).—Dielectric consts. were determined for oxides of Mg, Ba, Al, Ce, Zr, Th, Ta, Sb, Bi, and Cr.

A. B. D. CASSIE.

Measurements of the dielectric constants of salts. P. SCHUPP (Z. Physik, 1932, 75, 84—104).—Dielectric consts. were measured for the carbonates and nitrates of the alkali and alkaline-earth metals, and for the alkali chlorides; the relation of the results to the periodic table and refractive indices is discussed.

A. B. D. CASSIE.

Dipole moments of the naphthols. M. PUCHALIK (Physikal. Z., 1932, 33, 341—345).—The resonance method was used to find the dipole moments of α - and β -naphthol. The β -derivative has a higher moment than the α , and the moment of α -naphthol is lower than that of PhOH, whilst that of β -naphthol is lower than that of EtOH.

A. J. MEE.

Determination of the dielectric constant of liquid dielectrics, using the heterodyne method. K. HRYNAKOWSKI and S. KALINOWSKI (Rocz. Chem., 1932, 12, 225—231).—A description of apparatus for approx. determination of the dielectric const. of liquids.

R. TRUSZKOWSKI.

Determination of dielectric constants by the oscillatory circuit method. G. MÖNCH (Z. physikal. Chem., 1932, B, 16, 438—442).—In determining the dielectric const. of a gas or liquid with high-frequency oscillations a calibrated variable condenser is required to determine the change in capacity of a condenser when the dielectric is replaced by the substance under examination. This condenser may be calibrated in arbitrary units if the abs. val. of one const. is determined.
R. CUTHILL.

Dielectric measurements with organic dipole-free substances. G. BRIEGLEB (Z. physikal. Chem., 1932, B, 16, 276—283).—The dielectric const. and n of binary mixtures of C_6H_6 , CS_2 , CCl_4 , and heptane have been determined. The vals. for the two components of the displacement polarisation of the pure substances calc. by applying the mixture rule to the mixtures vary with concn., indicating that the electron frequencies and rotation-vibration frequencies are influenced by intermol. forces. C_6H_6 , CS_2 , $C_{10}H_8$, Ph₂, phenanthrene, *p*-dichlorobenzene, and *p*-xylene have zero dipole moment.
R. CUTHILL.

Dipole moment of *n*-propyl ether. L. MEYER and A. BÜCHNER (Physikal. Z., 1932, 33, 390—391).—The val. obtained is $1.16 \pm 0.05 \times 10^{-18}$ e.s.u.

A. J. MEE.
Association in dipole liquids. J. MALSCH (Physikal. Z., 1932, 33, 383—390).—The dependence of the dielectric const. of some highly-associated liquids (BuOH, EtOH, PrOH, H₂O) on temp., field strength, and frequency is discussed. It is possible to calculate the deviations from the normal as regards high-frequency effects due to association.

A. J. MEE.
Dielectric constant and power factor of some solid dielectrics at radio frequencies. W. ANDERSON (Phil. Mag., 1932, [vii], 13, 986—993).—Frequencies between 150 and 1500 kilocycles were used.
H. J. EMELÉUS.

Influence of substitution in naphthalene derivatives on, and comparison of dispersion of, magnetic rotation and birefringence. C. SALCEANU (Compt. rend., 1932, 194, 1227—1229).—The magnetic rotation at 150° compared with that of H₂O at 20°, and the magnetic birefringence compared with that of PhNO₂, both at 20°, have been determined for C₁₀H₈ and 10 derivatives. The influence of the substituents Me, Cl, Br, OH, NO₂, NH₂, and CN is similar to their effect in C₆H₆ (cf. A., 1907, ii, 727; J.C.S., 1896, 69, 1025), save as regards Me in 1-C₁₀H₇Me, where it is opposite. The dispersion of the rotation and birefringence between the green, yellow, and indigo lines of Hg for PhNO₂, 2-C₁₀H₇Me, and phenanthrene are approx. the same.

C. A. SILBERRAD.
Variation of the temperature constant and of Havelock's constant of magnetic birefringence for some fused organic substances. C. SALCEANU (Compt. rend., 1932, 194, 863—865).—Assuming that the optical magnetic anisotropies are independent of (a) temp, (b) λ , expressions are deduced (a) for the temp. const., holding only near the m. p., for C₁₀H₈, 2-C₁₀H₇Me, and phenanthrene; and (b) for Havelock's

const., decreasing with decrease in λ , for 2-C₁₀H₇Me and phenanthrene (cf. A., 1910, ii, 368; 1923, ii, 707).

C. A. SILBERRAD.
Rotatory dispersion of benzene solutions of α - and β -pinenes. J. RABINOVITCH (Compt. rend., 1932, 194, 1474; cf. this vol., 448).—The calculation of the amount of the third constituent has been corrected.
C. A. SILBERRAD.

Effect of solvents and temperature on the optical rotation of esters of menthyl and bornyl hydrogen xanthates and on menthyl and bornyl dixanthides. (MISS) I. M. McALPINE (J.C.S., 1932, 1016—1022).—Menthyl Me, menthyl Pr^{*β*}, menthyl CH₂Ph, menthyl *p*-nitrobenzyl, and bornyl Me xanthates and the menthyl and bornyl dixanthides were examined in 7 solvents; all showed strong anomalous rotation dispersion between 6716 and 4358 Å.

W. R. ANGUS.
Theory of anisotropic liquids. XV. Geometric optics of nematic substances. C. W. OSEEN (Ark. Matemat. Astron. Fysik., 1931, A, 22, 1—23; Chem. Zentr., 1931, ii, 3185—3186).—The path of the rays in the neighbourhood of a rectilinear thread of a nematic substance has been investigated.

L. S. THEOBALD.
Optical properties of mixed crystals; sodium ammonium and sodium rubidium tartrates. S. KOZIK (Bull. Acad. Polonaise, 1931, A, 247—266).—The properties of the double Na K, Na Rb, and Na NH₄ tartrates are tabulated. The refractive indices and mol. vols. increase slightly in the order given. The geometric properties of mixed crystals of Na tartrate with K, Rb, and NH₄ tartrates are similar to those of the pure tartrates. Refractive indices and densities are additive properties of the components.

J. W. SMITH.
Calculation of the refractive power of mixed immersion liquids. A. MAYRHOFER and F. WRATSCCHKO (Pharm. Presse, 1931, 33—35; Chem. Zentr., 1931, ii, 3232).—When no change in mol. condition occurs on mixing, $n = (V_1 n_1 + V_2 n_2) / (V_1 + V_2)$ as in the case of paraffin oil and 1-C₁₀H₇Br. In other cases n depends on the type of solution formed, and ultimately on the indices and densities of the components.

L. S. THEOBALD.
Variations in the optical constants of copper. H. LOWERY and R. L. MOORE (Phil. Mag., 1932, [vii], 13, 938—952).—Methods of measuring the optical consts. of polished metals are described and discussed.

H. J. EMELÉUS.
Physics of the nitrobenzene Kerr cell. V. Determination of electro-optical Kerr constant of nitrobenzene ($\lambda = 5461$ Å.). F. HEHLGANS (Physikal. Z., 1932, 33, 378—382; cf. A., 1931, 1220, 1355).—An interference method of determining the Kerr const. gives good agreement with others, the val. found being 3.86×10^{-5} e.s.u.
A. J. MEE.

Nature of the chemical linking. III. Transition from one extreme type of linking to another. L. PAULING (J. Amer. Chem. Soc., 1932, 54, 988—1003; cf. A., 1931, 1356).—The ionic and electron-pair linkings are discussed as examples of extreme types of linkings. As the parameters determining the nature of the atoms are changed, transitions from one type

to the other will take place continuously if the two possible electronic states are nearly degenerate and have the same multiplicity. If the multiplicities are different and the spin-orbit interaction of the electrons is negligible, the normal state may show a discontinuity at the crossing of two non-combining levels. The linking type may be determined from a consideration of electronic energy curves. The normal alkali halide mols. are essentially ionic; HF is largely ionic, and HCl, HBr, and HI have electron-pair linkings. The normal state of CO is a combination of a doubly- and a triply-linked structure, the latter being the more important. The types of linking formed by metals of the transition groups are also discussed.

G. M. MURPHY (c).

Electronic structures of polyatomic molecules and valency. R. S. MULLIKEN (Physical Rev., 1932, [ii], 40, 55—62).—The electronic structures of H_2O , NH_3 , CH_4 , CF_4 , Cl_4 , ClO_4' , SO_4'' , ClO_3' , SO_3'' , and CO_2 are briefly described in terms of one-electron wave functions.

N. M. BLIGH.

Interatomic distances in covalent molecules and resonance between two or more Lewis electronic structures. L. PAULING (Proc. Nat. Acad. Sci., 1932, 18, 293—297).—Tables of radii for non-metallic atoms in covalent mols., and radius sums and observed interat. distances from band spectra data for ICl, HCl, HBr, HI, H_2O , NH_3 , CH_4 , MeF, O_2 , CH_2O , N_2 , HCN, CN, and C_2H_2 are given. The effect of resonance among several equiv. structures is examined for N_2O , CO_2 , graphite, C_6H_6 , CO_3^- , NO_3^- , and the chemical properties of several org. mols.

N. M. BLIGH.

Quantum theory of the transference of energy of activation between molecules of the same kind. Fluorescent solutions. F. PERRIN (Ann. Physique, 1932, [x], 17, 283—314).—Mathematical. The interaction between a normal and an active atom is investigated and interpreted; the probable at. energy varies continuously, the energy transfer is discontinuous. The theory is extended to dissolved mols. and the action of the solvent.

N. M. BLIGH.

Structure of the isomeric diamminoplatinous chlorides. Discovery of a third isomeride. H. D. K. DREW, F. W. PINKARD, W. WARDLAW, and (in part) E. G. COX (J.C.S., 1932, 988—1004).—In place of Werner's *cis*- and *trans*-planar isomerides of $Pt(NH_3)_2Cl_2$, there are recognised 3 isomerides, which probably differ structurally. The reaction with phenoxtellurine dibisulphate shows that only the β -isomeride is a compound of bivalent Pt. The α -isomeride has 4 groups arranged round the Pt atom, but there is at present no evidence to show whether the distribution is tetrahedral or planar. The reactions with moist Ag_2O or aq. NaOH show that, whilst the β -isomeride gives a corresponding base, the α -isomeride gives a base which with HCl yields a β -isomeride, which can be transformed into the α -isomeride. The isomerides differ in colour, solubility, min. n , and X-ray diagrams. Formulæ have been assigned, and a mechanism is suggested for the transformation α -dichloride \rightarrow β -base is borne out by comparison with the behaviour of the corresponding α - and β -dipyridino-dichlorides, containing tert.

N. The α - and β -isomerides of $Pt(NH_3)_2Cl_2$ are also shown to be structural and not stereo-isomerides.

E. S. HEDGES.

Structure of simple and mixed tetramminoplatinous dihalides. H. D. K. DREW, F. W. PINKARD, W. WARDLAW, and (in part) E. G. COX (J.C.S., 1932, 1004—1016).—There is no definite evidence to show that the isomeric mixed tetrammines $Pt(NH_3)_2(C_5H_5N)_2Cl_2$ are *cis*- and *trans*-planar isomerides, as supposed by Werner. A study of their reactions indicates that the isomerism can be explained by assuming that the co-ordinate linkings between the NH_3 groups and Pt are paired. A tetrahedral arrangement is considered more probable.

E. S. HEDGES.

Connexion between chemical constitution and X-ray K absorption spectra. X. X-Ray spectroscopic investigation of structure of chemical complexes. II. O. STELLING (Z. physikal. Chem., 1932, B, 16, 303—337; cf. A., 1930, 671).—It is found experimentally that if a solid chloride of the first order exhibits two absorption edges in the Cl absorption spectrum, those of its complex compounds which contain non-ionisable Cl have edges at similar wave-lengths, whereas those compounds containing only ionisable Cl have only one edge. It has thus been possible to determine the structure of complex compounds of Fe^{II} , Co^{II} , Ni, Cu^{II} , and Cd chlorides. The harder edge is assumed to correspond with the ejection of a K electron from the Cl atom, and the softer with the transfer of an electron from the K to the M level. The difference between the two wave-lengths is a linear function of the at. no. of the metal for $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, and $CuCl_2$, although each wave-length rises to a max. and falls again as the at. no. increases. For geometrical isomerides with 2 Cl atoms in the complex, the soft edge corresponds with a longer wave-length for the *trans* form than for the *cis* form. The experimental conditions under which satisfactory K -absorption spectra may be obtained are examined. The most essential is suitable thickness of the absorbing material; with too thick layers structural details in the spectrum are obscured, and misleading simplicity results.

R. CUTHILL.

Magnetic resolution and nuclear moment of rhenium. P. ZEEMAN, J. H. GISOLF, and T. L. DE BRUIN (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 2—9).—A detailed account of work already noted (A., 1931, 1345).

Magnetisation of ferromagnetic powders. R. CHEVALLIER (Compt. rend., 1932, 194, 1327—1329).—The magnetic behaviour of a medium, e.g., basalt, in which ferromagnetic material is dispersed, in a weak field depends mainly on the form and dispersion of the particles of that material, in a strong one on the susceptibility of the non-ferromagnetic portion.

C. A. SILBERRAD.

Curie point of ferro-cerium. G. RASSAT (Compt. rend., 1932, 194, 1153).—Ferro-cerium containing 27.5% Fe loses its magnetism at about 40°; samples containing about 32% Fe do not cease completely to be magnetic up to the temp. of ignition, indicating the presence of more than one substance.

C. A. SILBERRAD.

Variability of magnetic ionic moment of some elements of the iron series. H. FAHLENBRACH (Ann. Physik, 1932, [v], 13, 265—296).—The susceptibilities of aq. solutions of NiCl_2 , CoCl_2 , and FeCl_3 , and of solutions of CoCl_2 in $\text{C}_5\text{H}_5\text{N}$ and EtOH , and their dependence on temp. and concn. were determined, and the variation of susceptibility with temp. of H_2O , EtOH , COMe_2 , and $\text{C}_5\text{H}_5\text{N}$. The relationship of susceptibility to temp. for COMe_2 and EtOH is linear; for $\text{C}_5\text{H}_5\text{N}$ it is independent of temp. There is no simple connexion between paramagnetism and colour. The dependence of magnetic ionic moment on concn. is investigated.

A. J. MEE.

Mechanism of intermolecular forces in organic compounds. II. G. BRIEGLEB (Z. physikal. Chem., 1932, B, 16, 249—275; cf. A., 1931, 1214).—The equations for the Kerr const. deduced by Langevin and Born's theory and by Gans may be applied to liquids if the polarisability anisotropies of the mol. in the gaseous state are replaced by the vals. for the condensed state. Kerr consts. of various org. compounds dissolved in non-polar solvents have been determined. The consts. deduced from the mol. Kerr consts. at infinite dilution are all less than those for the gaseous state, which is attributed to the presence in the solutions of "swarms" of solvent and solute mols. more or less oriented in relation to each other. From the variation with concn. of the mol. Kerr const., K , of non-polar substances without polar groups dissolved in an indifferent solvent, it appears that the orientation of these mols. relative to each other in the condensed state is determined by the polarisability anisotropy, as well as by the mean polarisability itself; the greater is the abs. anisotropy, the more pronounced is the orientation. From the variation with concn. of K and the mol. polarisation the relative orientations in associated complexes of mols. containing a single polar group may be deduced. With mols. containing several polar groups, the association will be such that the max. possible no. of polar groups saturate each other, or the groups with the largest moments are brought into proximity. The types of linkings effective in mol. compounds are analysed.

R. CUTHILL.

Weiss' molecular field. K. HONDA (Z. Physik, 1932, 75, 352—362).—Weiss' hypothesis of an intense mol. field, magnetising to saturation the elementary regions of a ferromagnetic substance, is incompatible with experimental facts.

A. B. D. CASSIE.

Tetrahedral field of force of atoms. R. REINICKE (Ann. Guébbard-Séverine, 1930, 6, 141—150).—A theory of mol. structure on the basis of regular tetrahedral atoms is advanced.

J. W. SMITH.

Collision areas and shapes of carbon chain molecules in gaseous state: *n*-heptane, *n*-octane, and *n*-nonane. R. M. MELAVEN and E. MACK, jun. (J. Amer. Chem. Soc., 1932, 54, 888—904).—From viscosity measurements at 100—250° with *n*-heptane, *n*-octane, and *n*-nonane the collision areas are calc. to be 26.7, 34.9, and 42.5 Å.², respectively. The shadowgraphic collision areas of various mol. models agree well with the calc. vals. if C chain compounds are assumed to coil into helical shapes. Vogel's empirical equation $c=1.47T_b$ is not valid for large mols.

E. J. ROSENBAUM (c).

Quantum-theoretical calculation of molecular linking energies. II. H. WEYL (Nachr. Ges. Wiss. Göttingen, 1931, 33—39; Chem. Zentr., 1932, i, 173).

X-Ray reflexion from inhomogenously strained quartz. C. S. BARRETT and C. E. HOWE (Physical Rev., 1932, [ii], 39, 889—897). N. M. BUGH.

Chemical reactions between metal sulphides and anticathode metals observed in photographs of the $K\beta$ spectrum of sulphur. B. SVENSSON (Z. Physik, 1932, 75, 120—128).—The S of metal sulphides deposited on anticathodes may form sulphides with the metals of the anticathode; the transition of S from one metal to another is revealed by changes in the $K\beta$ spectrum of S, and this gives a measure of the relative affinity of the two metals for S. Anticathodes used were Cu, Ag, Fe, and Al.

A. B. D. CASSIE.

Affinity. LVII. Diagram of state of pyrites, magnetic pyrites, troilite, and sulphur vapour, judged by vapour pressures, X-ray diagrams, densities, and magnetic measurements. R. JUZA and W. BILTZ (Z. anorg. Chem., 1932, 205, 273—286; cf. this vol., 239).—V. p.-composition curves have been determined at temp. from 629° to 1055°, the constitution of the solid phase being ascertained by X-ray analysis. The diagram consists chiefly of a two-phase region (saturated solution of FeS in FeS_2 + magnetic pyrites) in which the v. p. is nearly const., bounded on one side by a pyrites phase ($\text{FeS}_{2.04}$ — $\text{FeS}_{1.94}$), and on the other by a "troilite" phase ($\text{FeS}_{1.12}$ — $\text{FeS}_{1.02}$). Densities and magnetic susceptibilities were also determined. The latter increases linearly with composition from zero at $\text{FeS}_{1.94}$ to a max. (magnetic pyrites) at $\text{FeS}_{1.12}$, any further loss of S causing it to fall abruptly. This composition falls between the extreme compositions of the naturally occurring substance. No evidence of the existence of Fe_2S_3 or Fe_3S_4 was obtained.

F. L. USHER.

Cry of tin. B. CHALMERS (Nature, 1932, 129, 650—651).—When single-crystal wires of Sn or Cd are stretched no sound is produced during the gliding stage of extension, but the twinning which succeeds is accompanied by the characteristic "cry." The same sound also occurs when such wires are bent or violently twisted. The cry also occurs with polycryst. cast Sn or Cd, but drawn wires of small diameter do not give it unless annealed; the production of sound apparently depends on the size of the crystallites being greater than a min. Thermal measurements indicate that some of the mechanical energy supplied to the lattice to cause twinning is afterwards liberated as heat and, in some cases, as sound energy. A "cry" can be produced from Zn which twins readily, but no sound has been produced from metals which show no twinning.

L. S. THEOBALD.

Cry of tin. E. N. DA C. ANDRADE (Nature, 1932, 129, 651).—A discussion (cf. preceding abstract).

L. S. THEOBALD.

Fatigue of single crystals of pure metals. H. J. GOUGH (Erste Mitt. neuen Int. Verband. Materialprüf., 1930, A, 133—144; Chem. Zentr., 1932, i, 177—178).

Sudden translation of zinc crystals. E. SCHMID and M. A. VALOUCH (*Z. Physik*, 1932, 75, 531—538).—After slight extension a sudden translation occurs within the Zn crystals, probably due to a relaxation effect.
A. B. D. CASSIE.

Grating theory of ionic crystals. M. BORN and J. E. MAYER (*Z. Physik*, 1932, 75, 1—18).—The power law of repulsive potential is replaced by an exponential law, which, together with the attractive dynamic polarisability forces, explains the difference in stability of the NaCl and CsCl types.
A. B. D. CASSIE.

Grating energy of the alkali halides and the electron affinity of the halogens. J. E. MAYER and L. HELMHOLTZ (*Z. Physik*, 1932, 75, 19—29).—The method of the preceding abstract is applied to the alkali halides. Calc. electron affinities are: F 95.3, Cl 86.5, Br 81.5, and I 74.2; an accuracy of 2% is claimed.
A. B. D. CASSIE.

Growth-forms of metal crystals. G. TAMMANN and K. L. DREYER (*Z. anorg. Chem.*, 1932, 205, 77—80).—Cu separates from a dil. solution in Bi in angular crystals, but from a conc. solution in rounded ones. From a 25% solution rounded crystals are formed by slow (1° per min.), and angular by rapid (40° per min.), cooling. Similar differences were noted with Ag in Pb, and with Zn in Sn, Pb, or Cd, the behaviour in the case of Zn being independent of the solvent.
F. L. USHER.

Arrangements of the micro-crystals in copper and gold deposited by electrolysis. H. HIRATA and Y. TANAKA (*Mem. Coll. Sci., Kyoto*, 1932, 15, 9—22).—The deposits were examined by X-rays by the "transmission" method. Micro-crystals of Au are not deposited with any regularity.
W. R. ANGUS.

Secondary structure and mosaic structure of crystals. F. ZWICKY (*Physical Rev.*, 1932, [ii], 40, 63—77; cf. this vol., 12).—The relation of the mosaic to the secondary structure, and factors affecting the formation of thermally stable configurations, are discussed.
N. M. BLIGH.

Determination of the parameter of calcite by the temperature effect. E. FUKUSIMA (*J. Sci. Hiroshima Univ.*, 1931, A, 1, 195—201).—Laue photographs at 16°, 300°, and 600° confirm Tsuboi's results (*A.*, 1927, 400).
C. W. DAVIES.

Solid solutions [obtained] by precipitation and isomorphism between complexes of platinum and of quadrivalent tellurium. I. Structure of the chloroplatinates of caesium and of rubidium. G. NATTA and R. PIRANI (*Atti R. Accad. Lincei*, 1932, [vi], 15, 92—99).—An X-ray investigation of Cs₂PtCl₆ and of Rb₂PtCl₆ shows that both compounds are cubic, with 4 mols. in unit cell. Data: Cs₂PtCl₆, a 10.15 ± 0.01 Å., v 1045.7 × 10⁻²⁴ c.c., d 4.25; Rb₂PtCl₆, a 9.83 ± 0.01 Å., v 949.85 × 10⁻²⁴ c.c., d 4.04. Both compounds belong to the space group O_h^2 , and have the same type of structure as K₂PtCl₆. The val. of the parameter u which defines the position of the Cl ions is about 0.23—0.24 in the case of the Cs compound.
O. J. WALKER.

Organic molecular compound with a small unit cell. K. SCHNEIDER (*Z. physikal. Chem.*, 1932,

B, 16, 460—464).—The unit cell of the compound of acenaphthene and styphnic acid has I_a 9.05, I_b 14.8, and I_c 6.8 Å., and contains 2 mols. The mols. cannot be arranged according to the three-dimensional alternation principle.
R. CUTHILL.

Rotational motion of chain molecules in normal paraffins in the neighbourhood of their melting points. A. MÜLLER (*Naturwiss.*, 1932, 20, 282—283).—Near their m. p. mols. of normal paraffins show considerable vibration and rotation; the phenomena are discussed.
W. R. ANGUS.

X-Ray diagram of "hendecamethyltriase" from cellulose. C. TROGUS (*Naturwiss.*, 1932, 20, 317).—X-Ray measurements are given for the compound of which osmotic pressure was measured previously (cf. *ibid.*, 316).
W. R. ANGUS.

Plasticity of micellar systems, especially of cellulose. H. MARK (*Papier-Fabr.*, 1932, 30, 197—205).—The plastic behaviour of cryst., amorphous, and micellar systems is discussed, and the changes in the typical X-ray diagrams of cellulose and cellulose derivatives produced as a result of plastic flow and orientation of the micelles are described. The effect of swelling, temp., H₂O content, etc. on the behaviour of filaments or strips of cellulose acetate and nitrate during stretching, and the significance of the usual load-extension diagrams given by these and other cellulose materials are also discussed. Approx. formulæ give quant. expression to the stress-strain curves.
B. P. RIDGE.

Crystal structure and molecular configuration of simple derivatives of tetramethylmethane. I. Tetrachloro-, tetrabromo-, and tetra-iodohydrins of pentaerythritol. G. WAGNER and G. DENGEL (*Z. physikal. Chem.*, 1932, B, 16, 382—396).—The crystals belong to the class C_{2h} , the vals. of I_{100} , I_{010} , and I_{001} being: C(CH₂Cl)₄, 6.91₂, 6.28₉, 5.49₂; C(CH₂Br)₄, 7.19₉, 6.32₅, 5.71₉; C(CH₂I)₄, 7.55₂, 6.43₉, 6.07₅ Å. The space-group is C_{2h}^1 and the unit cells contain 1 mol. From the small vols. of the unit cells, the packing of the atoms in the mols. is closer than is compatible with a tetrahedral structure. It is probable that the 4 halogen atoms lie in a plane which intersects the plane containing the 4 C atoms in the two-fold axis, at the intersection of which with the planes of symmetry lies the central C atom.
R. CUTHILL.

Cristobalite structures. I. High-cristobalite. T. W. BARTH (*Amer. J. Sci.*, 1932, [v], 23, 350—356).—Contrary to previous work (*A.*, 1925, ii, 638) high-cristobalite has the space-group $P2_13$ (T^4). The unit cube has 8 mols. of SiO₂.
N. H. HARTSHORNE.

Artificial spherulites and related aggregates. H. W. MORSE, C. H. WARREN, and J. D. H. DONNAY (*Amer. J. Sci.*, 1932, [v], 23, 421—432).—Many inorg. substances have been obtained in the form of spherulites by pptn. in jellies. Their optical characteristics are described.
C. W. GIBBY.

Spherulite optics. H. W. MORSE and J. D. H. DONNAY (*Amer. J. Sci.*, 1932, [v], 23, 440—461).—Theoretical.
C. W. GIBBY.

Electrostriction of benzene. M. PAUTHENIER and O. DELAHAYE (Compt. rend., 1932, 194, 1465—1466).
C. A. SILBERRAD.

Hall effect in gold-silver alloys. E. VAN AUBEL (Z. Physik, 1932, 75, 119; cf. Ornstein and Geel, this vol., 12).—Attention is directed to the relation of the Hall effect to Ettinghausen and thermoelectric effects.
A. B. D. CASSIE.

Mechanism of electrical discharge in solid insulators. III. Electric strength and crystal structure. A. VON HIPPEL (Z. Physik, 1932, 75, 145—170).—The electrical strength of 11 NaCl type crystals was determined by a method that eliminates boundary effects; this method showed the strengths to be greater than present available vals. Dependence on orientation was also studied, and rules are given for relating strength to size, charge, and polarisability of the constituent ions, and to the hardness of the crystal.
A. B. D. CASSIE.

Magnetic properties of iron and its most important alloys. O. VON AUWERS (Naturwiss., 1932, 20, 257—264).—Magnetisation curves for different forms of Fe and its alloys are illustrated and discussed.
J. W. SMITH.

Magnetic properties of matter in strong magnetic fields. III. Magnetostriction. IV. Method of measuring magnetostriction in strong magnetic fields. V. Magnetostriction in dia- and para-magnetic substances. P. KAPITZA (Proc. Roy. Soc., 1932, A, 135, 537—555, 556—567, 568—600).—III. The general theory of magnetostriction is revised, mainly from the point of view of the thermodynamic relations and the requirements of crystal symmetry. There are three types of magnetostriction, the classical, at., and thermal, due respectively to the stress of magnetic lines of force, to the disturbance of the magnetic properties of the substance produced by the magnetic field, and to change of temp. The last-named type appears only in adiabatic magnetisation. Moduli or consts. of different orders for adiabatic and isothermal magnetostriction are defined.

IV. An extensometer is described for measuring changes of length down to 10^{-7} cm. in a short interval of time. The accuracy of the measurements and the possible stray effects when the apparatus is applied to the measurement of magnetostriction in strong magnetic fields are discussed.

V. Experiments on Bi crystals are described. In weak magnetic fields at all temp. and for all orientations of the crystal the magnetostriction follows the square law, having a positive sign along the trigonal axis and a negative sign perpendicularly. In strong fields at low temp. a saturation effect is observed. The influence of crystal orientation, impurities, and stress is discussed. An at. magnetostriction is also found in Sb, Ga, graphite, and probably Sn and W; and the limits of a possible magnetostriction are established for Be, Mg, and rock-salt. In general, the most marked effect occurs in those diamagnetic substances having a crystal lattice of low symmetry which change their resistance considerably in magnetic fields. The difficulty of applying the modern theory

of diamagnetism to account for the observed phenomena is discussed, and certain new hypotheses are suggested to explain the results.

L. L. BIRCUMSHAW.

Magnetic transformation of ferromagnetic metals. R. RUER (Z. anorg. Chem., 1932, 205, 230—234; cf. A., 1927, 925).—Heating and cooling curves have been redetermined with very pure Fe, and earlier results confirmed. The arrest on the heating curve is, however, 2° higher than that on the cooling curve.
F. L. USHER.

Influence of adsorbed surface films on the strength of fine quartz fibres. S. SCHURKOV (Physikal. Z. Soviet Union, 1932, 1, 123—131).—The strength per unit cross-section increases with decreasing cross-section, and is lowered by adsorbed vapours.
H. J. EMELÉUS.

Influence of foreign particles on cohesion limits and ultramicroscopic sol formation of synthetic rock-salt crystals. II. Single and mixed states of alkaline-earth chlorides. H. SCHÖNFELD (Z. Physik, 1932, 75, 442—467).—Large increases of the cohesion limits appear when CaCl_2 and SrCl_2 disperse as mols. throughout the crystal; the chlorides (MgCl_2 , BaCl_2) that form ultramicroscopic particles have little or no effect. Elastic limits, and stresses at breaking point were studied.
A. B. D. CASSIE.

Evaporation of incandescent wires in vacuum. II. L. PRÁSNÍK (Z. Physik, 1932, 75, 417—420; cf. A., 1931, 1106).—Numerical applications of the theory are made for W.
A. B. D. CASSIE.

Determination of mol. wt. by Horstmann's combination of vapour-pressure measurements. II. Vapour pressures and vapour densities of aluminium halides. W. FISCHER and O. RAHLFS [with B. BENZE] (Z. anorg. Chem., 1932, 205, 1—41; cf. A., 1930, 142).—Densities of unsaturated and saturated vapours of AlCl_3 , AlBr_3 , and AlI_3 have been determined, and v. p. of the same substances have been obtained between 10 and 700 mm. by four different methods. Heats of evaporation and sublimation are calc. The only mol. species present in the vapours are AlX_3 and Al_2X_6 . Cryst. AlCl_3 possesses a constitution different from that of the other two solids. Details of technique generally suitable for substances sensitive to traces of moisture or air are described.
F. L. USHER.

Relations between fundamental physical constants. R. T. BIRGE (Science, 1932, 75, 383).—A crit. discussion (cf. this vol., 444).
L. S. THEOBALD.

Thermal properties of tantalum. C. L. UTTERBACK and L. A. SANDERMAN (Physical Rev., 1932, [ii], 39, 1008—1011; cf. A., 1929, 1212).—The total radiation from very pure Ta was measured from 1000° to 2220° abs. A spectral temp. scale, $\lambda=0.667 \mu$, is given up to 2100° abs. The variation of resistance was measured up to 2600° , and the thermoelectric power with Pt up to 692° abs.
N. M. BLIGH.

Superconductivity. K. CLUSIUS (Z. Elektrochem., 1932, 38, 312—326).—A review.

Measurements with liquid helium. XVI. Superconductivity of carbides, nitrides, borides,

and silicides. W. MEISSNER, H. FRANZ, and H. WESTERHOFF (Z. Physik, 1932, 75, 521—530).—Resistance down to 1.2° abs. was determined for Ti, Zr, Hf, Ta, and Fe carbides, Ti and Zr nitrides, Hf, Ti, and Zr borides, and for Ta silicide and the mixed crystals Fe-Si and Ni-Si. Carbides, nitrides, borides, and silicides of the heavier metals become superconductive, but transition temp. are lower for the last two.

A. B. D. CASSIE.

Energy exchanges between molecules. P. S. H. HENRY (Proc. Camb. Phil. Soc., 1932, 28, 249—255).—An explanation of the discrepancy between the sp. heats at high temp. of the diat. gases as found by sound velocity measurements and by calculation is examined on the evidence of a shorter period of relaxation for the vibrational energy than the previously accepted val.

N. M. BLIGH.

Accurate determination of physico-chemical constants at very high temperature. F. M. JARGER (Bull. Soc. chim. Belg. 1932, 41, 30—52).—A lecture, dealing especially with the determination of the sp. heats of solids at temp. up to 1625°, and of the surface tension and electrical conductivity of liquids up to 1650°. The significance of the variation with temp. of the sp. heats of the metals is reviewed.

H. F. GILLBE.

Vapour-pressure constant of ammonia, entropy of crystalline ammonia, and the reaction $N_2 + 3H_2 = 2NH_3$. T. E. STERNE (Physical Rev., 1932, [ii], 39, 993—1007; cf. A., 1931, 1222).—Mathematical. An expression for the v.-p. const. of an NH_3 mol. is calc. by statistical quantum mechanics, and evaluated for ordinary temps. as -1.55. For the reaction $2NH_3 \rightarrow N_2 + 3H_2$ between the cryst. phases at abs. zero there is an increase in entropy of $(9R/4) \log 3$.

N. M. BLIGH.

Density of carbon monoxide. At. wt. of carbon. E. MOLES and M. T. SALAZAR (Anal. Fis. Quím., 1932, 20, 182—199).—The mean normal density of CO, prepared from HCO_2Na , HCO_2H , and from $K_4Fe(CN)_6$ is 1.25010 g. per litre; the at. wt. of C is thus 12.006, in conformity with the suggestion that there exists an isotope of C of at. wt. 13.

H. F. GILLBE.

Specific volume of water between 20° and 650° and of ethyl ether and ethyl alcohol between 20° and 400°, at pressures of 1—2500 kg. per sq. cm. G. TAMMANN and A. RÜHENBECK (Ann. Physik, 1932, [v], 13, 63—79).—Vol. and dilatation isotherms and isobars are given. The max. and min. dilatation above and below the crit. temp. are considered.

W. R. ANGUS.

Pressure variation of the heat function as a direct measure of the van der Waals forces. F. G. KEYES and S. C. COLLINS (Proc. Nat. Acad. Sci., 1932, 18, 328—333).—A direct method of measuring the change of thermodynamic potential with pressure at const. temp. and results for CO_2 and NH_3 are given. Good agreement with vals. calc. from the equation of state is obtained.

N. M. BLIGH.

Heat of vaporisation of water at 50°, 70°, and 90°. E. F. FLOCK and D. C. GINNINGS (Bur. Stand. J. Res., 1932, 8, 321—324).—The latent heat at 50°,

70°, and 90° is 2381.6, 2333.6, and 2283.4 international joules per g., respectively. These agree with the vals. obtained by extrapolating the data for temp. > 100°.

J. W. SMITH.

Collision area of the gaseous carbon tetrachloride molecule. E. H. SPERRY and E. MACK, jun. (J. Amer. Chem. Soc., 1932, 54, 904—907).—From viscosity data for CCl_4 between 50° and 250°, the Sutherland const. was calc. to be 335 and the collision area 22.0 sq. Å. The radius of the Cl atom domain is estimated to be 1.2 Å.

E. J. ROSENBAUM (c).

Fluidity method for the determination of association. I. E. C. BINGHAM and L. W. SPOONER (J. Rheology, 1932, 3, 221—244).—The fluidities and d of the following compounds have been measured at 0°, 10°, 20°, 30°, 40°, 60°, 80°, and 100°: *n*-amyl ether, isoamyl ether, Bu^a_2O , $(CH_2Ph)_2O$, tri-*n*-amylamine, triisoamylamine, NBu^a_3 , *m*- $NH_2 \cdot C_6H_4Me$, and eugenol. Published data have been used for a revision of the at. temp. const. for H, O, Cl, Br, I, S, N, and CH_2 . Tables are given, from which it is possible to find the abs. temp. required to give any compound made up of these atoms any desired fluidity.

E. S. HEDGES.

The α and β solid solutions of copper-zinc alloys and corresponding liquid solutions in equilibrium with them examined thermodynamically. F. H. JEFFERY (Trans. Faraday Soc., 1932, 28, 452—455).—Existing equilibrium data suggest that the α and β solid phases are solutions of $CuZn_4$ and $CuZn_2$, respectively, in monat. Cu, in equilibrium with a liquid solution of $CuZn_4$ in monat. Cu. The conclusions are discussed in relation to the X-ray data for the Cu-Sn system (A., 1929, 987; 1931, 418).

J. G. A. GRIFFITHS.

Constitution of liquid and solid alloys of the copper-gold system examined thermodynamically. F. H. JEFFERY (Trans. Faraday Soc., 1932, 28, 455—457).—The co-existing liquid and solid alloys consist of monat. Cu and monat. Au.

J. G. A. GRIFFITHS.

Silver-copper alloys. W. BRONIEWSKI and S. KOSLACZ (Compt. rend., 1932, 194, 973—975).—Curves are given to show the relation between the composition of alloys annealed at 650° and fusibility, conductivity, temp. coeff. of resistance, thermoelectric power and its variation with temp., electrode potential in aq. $CuSO_4$ (cf. A., 1898, ii, 582), and various mechanical properties. The eutectic, m. p. 779°, contains 71% Ag; the max. solubility of Ag is 7% of Cu 6% (cf. A., 1931, 556); when slowly cooled 1% of either remains in solution. Annealing improves all the alloys, which if prepared in a reducing atm. are malleable, but if fused in an oxidising atm. are affected by Cu_2O .

C. A. SILBERRAD.

System gold-mercury. I. N. PLAKSIN (Arb. Staats-Univ. Fernen Ostens, 1929, 7, (13); Z. Metallk., 1932, 24, 89).—The system contains two compounds, Au_2Hg and $AuHg_2$. The latter decomposes at 310° into Au_2Hg and liquid; $AuHg_2$ is stable up to 420° and undergoes a polymorphic transformation at 402° in alloys with 51—84 at.-% Au. A second transformation occurs in alloys with 1.3—37 at.-% Au at 122°

with a max. heat effect at 32.5—36.1 at.-% Au, and a third transformation at -36° in alloys with up to 66.6 at.-% Au. The eutectic lies at -38.89° and $<0.1\%$ Au. When the alloy corresponding with AuHg_2 is melted and allowed to solidify the lower layers have a higher Au content than the upper (40 against 33 at.-%), but small crystals of AuHg_2 may be isolated from the upper layers. A. R. POWELL.

Lattice spacings of iron-aluminium alloys. A. J. BRADLEY and A. H. JAY (Iron and Steel Inst., May, 1932, advance copy).—The lattice spacings of Fe-Al alloys between 0 and 33% Al have been determined by an improved powder method. Although all the alloys lie within the Fe-rich α -solid solution field in the diagram of Gwyer and Phillips, the lattice spacings agree with Vegard's law only when Al $<10\%$. Between 10 and 17% Al, annealed alloys have const. lattice spacings and a lattice arrangement which is based on the compound Fe_3Al . Between 17 and 20% Al, annealed alloys show a slight decrease in lattice spacing and the structure tends towards the FeAl type. Quenched alloys up to 14% Al have random lattice structure with increasing lattice spacing, but at this point there is a sudden fall in lattice spacing corresponding with the formation of the FeAl type of structure. The spacing between 14 and 20% Al in quenched alloys is somewhat variable. Alloys with $>20\%$ Al, whatever the heat treatment, contain the FeAl type of lattice with increasing lattice spacing as the Al content rises. E. H. BUCKNALL.

X-Ray investigation of bismuth-antimony alloys. E. G. BOWEN and W. M. JONES (Phil. Mag., 1932, [viii], 13, 1029—1032).—Bi-Sb alloys maintained above the m. p. of Bi, and cooled slowly, become homogeneous, and show an almost linear change of lattice edge with composition over the whole range of compositions. H. J. EMELÉUS.

Effect of hot rolling on mechanical properties of yttrium alloy. T. WATASE (Suiyokai-Shi, 1931, 6, 631—638).—Yt alloy should be hot-worked to one third of the original section to obtain a strength of 40 kg. per sq. mm. and elongation more than 15%. Mg (0.5—1.0%) has less effect on the mechanical properties, but addition of Si up to 0.67% lowers the ductility and caused cracking on rolling.

CHEMICAL ABSTRACTS.

[Spontaneously] hardening alloys of lead, nickel, and cadmium. B. GARRE and A. MÜLLER (Z. anorg. Chem., 1932, 205, 42; cf. A., 1931, 900).—When quenched from 220° alloys of Pb, Ni, and Cd behave similarly to those of Pb, Sb, and Cd previously described. The hardening effect increases with duration of heating. Pb alloyed with NiCd_4 is less resistant to conc. H_2SO_4 , but more resistant to 10% acid, than pure Pb. F. L. USHER.

Silumin containing copper. N. KAWASHIMA (Suiyokai-Shi, 1931, 6, 585—592).—The hardness and tensile strength of silumin increase and the elongation decreases with increase in Cu content up to 4%. Salt-water corrosion is diminished.

CHEMICAL ABSTRACTS.

Equilibrium diagram of the aluminium-rich aluminium-tin-nickel system. S. KATO (Suiyo-

kai-Shi, 1931, 6, 529—533).—Alloys containing up to 5% Sn and 10% Ni were studied; a binary eutectic line liquid $\rightleftharpoons \text{Al} + \text{Al}_3\text{Ni}$ and a ternary eutectic point liquid $\rightleftharpoons \text{Sn} + \text{Al} + \text{Al}_3\text{Ni}$ were found at 270° at the Sn corner of the equilibrium diagram.

CHEMICAL ABSTRACTS.

Conditions of applicability of Trouton's rule to liquid mixtures and solutions. A. KIREEV (J. Gen. Chem. Russ., 1931, 1, 1057—1061).—Trouton's rule is applicable to normal liquid mixtures for which the ratio of the partial pressure of a component to its mol. concn. is const. The formation of compounds leads to an increase in the val. of Trouton's coeff., K_s , when the concn. of the component in question is diminished. Dissociation of a component leads to opposite effects. In mixtures of associated liquids the val. of K_s may remain const. or may vary, according to the nature of the given mixture.

R. TRUSZKOWSKI.

Composition of vapours from boiling binary solutions. D. F. OTHMER (Ind. Eng. Chem. [Anal.], 1932, 4, 232—234).—An improved method (cf. A., 1928, 943) and apparatus for determining vapour composition curves and the elevation of the b. p. of solutions are described. Results are given for C_6H_6 -AcOH, H_2O - HCO_2H , and AcOH- Ac_2O . The C_6H_6 -AcOH mixture has an azeotropic composition at 98.5% of C_6H_6 .

E. S. HEDGES.

Measurement of the diffusion constant. Y. NISIZAWA (Bull. Chem. Soc. Japan, 1932, 7, 72—84).—When a solid or conc. solution is placed at the bottom of a vertical column of solvent and allowed to diffuse upwards for a time t , it may be shown that $\log c_1/c_2 = (x_1^2 - x_2^2)/4Dt$, where c_1 and c_2 are the concns. at heights x_1 and x_2 , respectively, and D is the diffusion const. By this method, D has been determined for KI, BaCl_2 , CaCl_2 , EtOH, COMe_2 , carbamide, glycerol, pepsin, and various org. acids, dyes, sugars, soaps, and cellulose derivatives, the changes in concn. being followed by means of sp. gr. beads. Irradiation and preliminary heating cause an increase in the rate of diffusion of cellulose nitrate, indicating an increase in the degree of dispersion. D. R. DUNCAN.

Influence of magnetic field on crystallisation. D. SAMURACAS (Compt. rend., 1932, 194, 1225—1227).—The crystallisation of solutions of FeSO_4 , NiSO_4 , CoCl_2 , CuSO_4 , and MgSO_4 is accelerated by a magnetic field. C. A. SILBERRAD.

Application of Dühring's relation to solubilities. R. L. HARRIS (Ind. Eng. Chem., 1932, 24, 455—457).—The solubilities of inorg. salts in H_2O are shown to vary with temp. in accordance with an empirical formula which is analogous to Dühring's formula for v.-p. variations. J. G. A. GRIFFITHS.

Solubility in the solid state and atomic dimensions of the oxides of the bivalent, trivalent, and quadrivalent metals. L. PASSERINI (Gazzetta, 1932, 62, 85—101).—The cubic oxides of Ni, Mg, Co, Mn, Cd, and Ca are completely miscible in the solid state only provided that the radius of the larger cation does not exceed that of the smaller one by more than 12%. For differences up to 29% there is only partial miscibility and the max. amount of

dissolved oxide varies inversely as the % difference of the radii of the two cations. For differences of 30% and upwards miscibility in the solid state is no longer possible. Analogous relations are found when the miscibility is compared with the % difference in the mol. vol. of the two oxides. The rhombohedral oxides of Al, Fe, and Cr behave similarly both qualitatively and quantitatively, but in the case of the cubic oxides of Th, Co, Hf, and Zn the limits of complete and partial miscibility are about 1–2% higher. The solid solutions were mostly obtained at temp. well below the m. p. or sublimation point of the oxides.
O. J. WALKER.

Behaviour of polonium during crystallisation of metals. G. TAMMANN and A. VON LÖWIS OF MENAR (*Z. anorg. Chem.*, 1932, 205, 145–162).—The solubility of Po in Bi, Te, Sn, Sb, or Cd is of the order $5 \times 10^{-10}\%$. Po does not exhibit enhanced solubility in cryst. metal tellurides. During crystallisation Po begins to separate at temp. considerably higher than the m. p. of the poly-eutectic.

F. L. USHER.

Mechanism of dissolution of organic substances in non-aqueous liquids. I. Cellulose nitrate and acetone. C. TROGUS, T. TOMONARI, and K. HESS. II. Formation of celluloid. K. HESS, T. TOMONARI, and C. TROGUS (*Z. physikal. Chem.*, 1932, B, 16, 351–373, 374–381).—I. The dissolution of cellulose nitrate in binary mixtures of COMe_2 with benzene, alcohols, aromatic hydrocarbons, and H_2O has been investigated by X-ray examination of the solid phase and analysis of the liquid phase; two compounds of cellulose nitrate with COMe_2 are formed which lose COMe_2 in air. The amount of COMe_2 taken up by the solid phase for a given equilibrium concn. of COMe_2 falls as the temp. rises. It seems that for any medium to dissolve cellulose or its derivatives it must be able to form a compound with the substance to be dissolved, and also to dissolve this compound.

II. In ligroin solution *d*-camphor and cellulose trinitrate form a compound in which there is at least 1 mol. of camphor per C_6 mol.; this compound is sol. in many org. solvents. Commercial celluloid contains crystallites of camphor and of this compound, the latter being smaller than those formed in the cellulose trinitrate fibre.
R. CUTHILL.

System HIO_3 – HNO_3 – H_2O ; solubilities and viscosities. E. MOLES and A. PÉREZ VITORIA (*Anal. Fis. Quím.*, 1932, 30, 200–207).—The solubility of HIO_3 at 25° in HNO_3 solution rises continuously from about 1% in 65.30% HNO_3 to 10% in 43.32% HNO_3 and to 35.08% in 20.33% HNO_3 . The viscosity ($\text{H}_2\text{O}=1$) of aq. HIO_3 solutions rises at an increasing rate from 1.021 for a 3.2% solution to 1.650 for a 46% solution; there is no evidence of hydrate formation. The viscosity of HNO_3 solution is a max. at about 65.30% HNO_3 . The viscosity–composition diagram of the ternary system exhibits a min. which suggests the formation of a compound $\text{HIO}_3 \cdot 3\text{HNO}_3$.

H. F. GILLBE.

Influence of magnesium salts on the solubility of potassium and sodium chlorides. D. LANGAUER (*Rocz. Chem.*, 1932, 12, 258–269).—The solu-

bility of mixtures of NaCl and KCl at 25 – 105° has been determined in the presence of various concns. of MgCl_2 and MgSO_4 .
R. TRUSZKOWSKI.

Characteristics of vanillin and coumarin. R. M. HITCHENS.—See this vol., 615.

Kinetics and energetics of gas adsorption. H. FREUNDLICH (*Trans. Faraday Soc.*, 1932, 28, 195–201).—A general survey.
J. G. A. GRIFFITHS.

Kinetics of adsorption of hydrogen on platinum and nickel. E. B. MAXTED and N. J. HASSID (*Trans. Faraday Soc.*, 1932, 28, 253–261).—The magnitude of the slow process following the initial rapid adsorption increases with rise of the absorption temp. and then decreases to zero at the temp. of outgassing. The adsorptive power at a low temp. is increased by previously raising the temp. to a high val. without degassing. Repetition of the process increases the adsorption at the lower temp. to a const. val. An activation process is probably involved.
J. G. A. GRIFFITHS.

Heats of adsorption and kinetics of adsorption. W. E. GARNER (*Trans. Faraday Soc.*, 1932, 28, 261–269; cf. A., 1931, 1226).—Thermal and velocity data for adsorption processes are discussed (A., 1931, 1365). The equation developed for the diffusion process is of the same form as that for the velocity of activated adsorption, hence Kingman's results (see below) do not prove the absence of diffusion in the system H_2 –C.
J. G. A. GRIFFITHS.

Discontinuities in adsorption processes. A. J. ALLMAND, L. J. BURRAGE, and R. CHAPLIN (*Trans. Faraday Soc.*, 1932, 28, 218–222).—A summary and extension of the authors' recent work with charcoal and SiO_2 gel. With CCl_4 at 25° , the increments between successive breaks in the isotherms are almost const. The adsorption by charcoal of CS_2 – H_2O mixtures and of PhOH from H_2O is discontinuous.
J. G. A. GRIFFITHS.

Possible connexion between activated adsorption and gas displacement effects. A. J. ALLMAND and R. CHAPLIN (*Trans. Faraday Soc.*, 1932, 28, 223–226; cf. this vol., 331).—Existing data and fresh results with charcoal degassed at various temp. are in accord with the view that in many cases of adsorption the process requiring activation is the displacement of traces of residual gas from the adsorbing surface by the freshly-adsorbed mols. Examples of "activated adsorption" may well be cases of displacement phenomena.
J. G. A. GRIFFITHS.

Adsorption of hydrogen by charcoal. F. E. T. KINGMAN (*Trans. Faraday Soc.*, 1932, 269–272).—An account of previous work (A., 1931, 677, 1006).
J. G. A. GRIFFITHS.

Sorption of hydrogen by platinised charcoal. R. BURSTEIN and A. FRUMKIN (*Trans. Faraday Soc.*, 1932, 28, 273–275; cf. A., 1929, 640).—The adsorption of H_2 by sugar charcoal outgassed at 900° increases with rise of temp. and is therefore "activated." 0.2% of Pt increases the adsorptive capacity of the C.
J. G. A. GRIFFITHS.

Adsorption and reflexion processes in interaction of hydrogen and metals. K. F. BONHOEFFER and A. FARKAS (*Trans. Faraday Soc.*, 1932, 28, 242–

247; cf. A., 1931, 691; this vol., 28).—In confirmation of theory, the accommodation coeff.-temp. curves for H_2 on the clean and poisoned surfaces of a metal intersect. Corresponding with the discontinuity in the velocity of *para*- H_2 transformation on Ni, a discontinuity occurs in the accommodation curve at a certain density of adsorption. Similar discontinuities occur with Pt and Fe, thus indicating hydride formation. H_2 can be adsorbed on "O₂-covered charcoal" without adjustment of the *ortho*:*para* ratio, thus showing that the H_2 is adsorbed in the "mol." state and not in the "at." state characteristic of adsorption on metals in which the H atoms are more firmly bound to the metal than to each other.

J. G. A. GRIFFITHS.

Activated adsorption of hydrogen and the *para*-hydrogen conversion. H. S. TAYLOR and A. SHERMAN (Trans. Faraday Soc., 1932, 28, 247—253; cf. A., 1931, 678).—Data are presented for Ni, ZnO, ZnO-Cr₂O₃, Cd, CdO, MnO-Cr₂O₃, CuO-Cr₂O₃, and Al₂O₃ which show that surfaces at which activated adsorption of H_2 occurs exhibit at the same temp. parallel efficiencies in *ortho-para*- H_2 interconversion. No such parallelism exists between "van der Waals adsorption" and the interconversion process. The decrease of efficiency of the *para* → *ortho* change with rising temp. of charcoal is shown to be due to the bimol. nature of the surface process, the velocity of which decreases owing to increasing bareness of the surface at higher temp.

J. G. A. GRIFFITHS.

Adsorption and dissolution of gases by metals. A. F. BENTON (Trans. Faraday Soc., 1932, 28, 202—218; cf. A., 1930, 990; 1931, 902, 1005, 1225).—From existing and new equilibrium and velocity data for the sorption of N₂, H₂, and O₂ by Cu and Fe, and of H₂ by Ni, definite evidence has been obtained in all cases, except those involving N₂, that physical adsorption, activated adsorption, and a third process, probably dissolution, occur, and the contribution of each process to the total sorption has been determined. The differentiation among the three processes and the relation between activated adsorption and compound formation are discussed.

In the system Ag-O₂ between 174° and 200°, oxide formation occurs at sufficiently high pressures of O₂. The above three processes can be distinguished, however, in the sorption of O₂ at pressures below the dissociation pressure of the oxide (cf. A., 1929, 274).

J. G. A. GRIFFITHS.

Adsorption by humic acid. K. KAWAMURA (Utsonomiya Agric. Coll. Bull., 1931, No. 1; Proc. Internat. Soc. Soil Sci., 1932, 7, 14—15).—"Humic acid" obtained from peat by pptn. from alkaline solution and washing with EtOH and Et₂O forms definite "humates" with Ba(OH)₂ and NaOH from solutions >3 milli-equivs. per 100 c.c. Further addition of base is followed by its adsorption. Humus from sucrose behaves similarly. Crude humus both from peat and sugar reacts with AlCl₃ solution with the apparent formation of an Al trihumate. No Cl' is absorbed from the solution. Humic acid after treatment with AlCl₃ exhibits exchange acidity which increases with the amount of AlCl₃ used, reaching a

const. val. corresponding with the formation of a trihumate.

A. G. POLLARD.

Rates of condensation and evaporation in intensively dried systems. Effect of intensive drying on accommodation coefficient of liquid and solid surfaces for molecules of their own vapours. F. J. WILKINS (Phil. Mag., 1932, [vii], 13, 1014—1020).—The decrease in the rate of evaporation of NH₄Cl and EtBr on intensive drying, without alteration of the v. p. (cf. A., 1929, 636; this vol., 329), is attributed to a decrease in the accommodation coeff. of solid NH₄Cl and liquid EtBr for their own vapours.

H. J. EMELEUS.

Surface activity and orientation of polar molecules in relation to the nature of the phase boundary. VII. Capillary properties of aromatic amines and their salts. A. B. TAUBMAN (J. Gen. Chem. Russ., 1931, 1, 1039—1056).—The surface activity and adsorption of *p*-toluidine at the phase boundaries of H₂O and C₆H₆ or hexane are in close accordance with Langmuir's law, slight deviations from which are, however, encountered at the aq. solution-air interface. The mol. consts. of *p*-toluidine are the same at all boundaries, the length of the oriented mol. being 6.6×10^{-8} cm. and the area occupied by it at saturation 25.8×10^{-16} sq. cm. A method for the determination of the concn. of surface-active substances in solution is described which depends on the capillary-manometric measurement of surface tension. *p*-Toluidine is present partly as associated mols. in hydrocarbon solution. The above method is applied to determine the solubility of *p*-toluidine and *o*-, *m*-, and *p*-cresol in H₂O. Antonov's law (cf. A., 1907, ii, 606) is not applicable to the above systems.

R. TRUSZKOWSKI.

Water-jet affected by tobacco smoke. T. TERADA, S. TANAKA, and K. ITÔ (Nature, 1932, 129, 614—615).—A change produced by tobacco smoke in the shape of a H₂O jet, and explained by a lowering of the surface tension of H₂O, is described.

L. S. THEOBALD.

Accommodation coefficient of hydrogen; a sensitive detector of surface films. (Miss) K. B. BLODGETT and I. LANGMUIR (Physical Rev., 1932, [ii], 40, 78—104; cf. Knudsen, A., 1911, ii, 368).—An equation for the coeff. is derived. The effect on the coeff. of adsorbed films is investigated.

N. M. BLIGH.

Behaviour of picric acid, *p*-nitrophenol, and certain hydroxyanthraquinones towards vacuum-sublimed films of salts. J. H. DE BOER (Z. physikal. Chem., 1932, B, 16, 397—407).—Quinizarin vapour undergoes a surface reaction with a vac.-sublimed film of BaCl₂ on moderate heating similar to that of alizarin (this vol., 223), whereas picric acid vapour forms Ba picrate and displaces HCl, reaction ultimately proceeding through the whole thickness of the film. *p*-Nitrophenol vapour is strongly but reversibly adsorbed by films of BaCl₂ or CaF₂, the absorption spectrum in the adsorbed state being displaced towards longer wave-lengths.

R. CUTHILL.

Osmosis in binary systems in which [there are] two membranes. F. A. H. SCHREINEMAKERS

(Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1380—1387).—The theoretically possible phenomena are discussed. J. W. SMITH.

Abnormal osmosis at non-swelling membranes. III. K. SÖLLNER and A. GROLLMANN (Z. Elektrochem., 1932, 38, 274—282; cf. A., 1930, 688).—Abnormal osmosis is not due solely to variations of the sizes of the membrane pores, but may be caused also by other types of heterogeneity of the membrane such as result from a mosaic-like structure and occur frequently in natural membranes. Very great and rapidly established negative osmosis is observed with solutions of Li salts; in accordance with the theory, the effect is smaller with Na salts, whilst with K salts the negative effect reverses on increasing the thickness of the membrane. Details are given of the experimental verification of the theory. H. F. GILLBE.

Hydrogen-ion exchange and its regularities. R. W. BELING (Kolloid-Beih., 1932, 35, 265—330).—The amount of H⁺ exchange in H-permutite, humic acid, and MnO₂ with the cations of various salts depends on the amount of the added cation. A connexion with the nature of the cation, particularly its degree of hydration, is apparent only when secondary influences, such as hydrolysis and change in the degree of dispersion of the colloidal substance, are absent. The exchange is increased by rise of temp., but to different extents, depending on the cation; the influence of temp. is particularly strong in the weakly hydrated K⁺ and Ba⁺⁺. By repeated treatment with conc. solutions practically all the H⁺ can be exchanged. The process of cation exchange is investigated mathematically. E. S. HEDGES.

Anomalous electrical dispersion of polar solutions. R. GOLDAMMER (Physikal. Z., 1932, 33, 361—367).—The anomalous dispersion due to the mol. polarisation of Bu^αOH, Bu^βOH, and isoamyl alcohol in dil. solution has been investigated (1) for wave-lengths of 0.5—1.4 m. by Drude's second method, and (2) for wave-lengths of 25 and 250 m. by the resonance method. There is good qual. agreement between theory and experiment. A. J. MEE.

Cryoscopic study of ether and acetone in water and solutions of sodium chloride. E. BOURION and E. ROUYER (Compt. rend., 1932, 194, 1240—1242; cf. A., 1931, 910).—F.-p. data are recorded. C. A. SILBERRAD.

Cryoscopy of solutions containing more than one electrolyte. V. K. SEMENTSCHENKO and E. A. ZAVADA (J. Gen. Chem. Russ., 1931, 1, 1114—1124).—For the systems NaCl-NH₄Cl-H₂O and NaCl-(NH₄)₂Al₂(SO₄)₄-H₂O the f.-p. depressions are in accordance with the mixture rule for total concn. of 1.5—2*M*. In the presence of H⁺ anomalous results are obtained. For NaCl-NH₄Cl-HCl-H₂O and NaCl-HCl-H₂O the depressions are less than those calc. from the mixture rule. This rule is followed in all cases studied at the van't Hoff point, at which the osmotic coeff. and the activity factor of the solvent are equal to 1. R. TRUSZKOWSKI.

Colloidal properties of charcoal. I. Preparation and properties of the sol. H. LACHS and K. GESTLÓWNA (Rocz. Chem., 1932, 12, 213—224).—

Charcoal hydrosols are obtained by the action of H₂SO₄ on dry sucrose, the reaction mixture being diluted with H₂O after 24 hr., and purified by repeated ultrafiltration. The hydrogel so obtained yields sols in which the particles are negatively charged and consist of roughly spheroidal, amorphous masses containing 53% C. 70% of the particles have a diameter of about 144 μμ, 15% about 35 μμ, and the remainder about 4.4 μμ. R. TRUSZKOWSKI.

Constitution of gold sols. W. PAULI (Oesterr. Chem.-Ztg., 1932, 35, 79—80).—A lecture.

Validity of the Lambert-Beer law for colloids. B. LANGE (Z. physikal. Chem., 1932, 159, 277—294).—Measurements of the absorptive power of sols have been made by a new photo-electric method capable of measuring very small absorptions very accurately. Lambert's law for sols may be deduced from probability considerations, and the validity of the law has been fully confirmed experimentally by observations on Au sols and diluted Indian ink. The deviations reported by Soós (A., 1926, 575) must be ascribed to defective experimental technique. Beer's law has also been shown to be valid for a variety of colloids, and such deviations as occur with other colloids are attributable to variations in the degree of dispersity and similar causes. R. CUTHILL.

Solvation equilibrium in colloidal solutions. G. V. SCHULZ (Z. physikal. Chem., 1932, 159, 374).—A correction (cf. this vol., 225). R. CUTHILL.

Osmosis and solvation of disperse systems. W. OSTWALD (Z. physikal. Chem., 1932, 159, 375—392).—The equation $P = cRT/M + kc^n$, where *R* and *T* have their usual significance and *k* is a const., is suggested for the measured osmotic pressure, *P*, of a solution, of concn. *c*, of a substance of mol. wt. *M*. The first term represents the usual van't Hoff pressure and the second a swelling or solvation pressure, the val. of *n* usually being about 2 (cf. A., 1918, ii, 391). This equation, which may be deduced both thermodynamically and by mol.-kinetic considerations (cf. A., 1929, 1380; 1931, 1230), agrees well with available data for the osmotic pressure of sols and of mol. dispersions up to the highest concns. For dil. sols the second term becomes zero, whilst for conc. sols the first term is negligible compared with the second (cf. this vol., 225). R. CUTHILL.

Behaviour of disperse systems in filtered ultra-violet light. K. BORGMANN (Süddeut. Apoth.-Ztg., 1931, 71, 70—72; Chem. Zentr., 1932, i, 190).—BaPt(CN)₄ does not fluoresce in solution, whilst the fluorescence of a solution of hydrastinine hydrochloride is stronger than that of the solid. The difference is not due to the formation of a colloidal solution. The fluorescence is associated with mol. aggregates. A solution of BaPt(CN)₄ and gelatin is strongly fluorescent, even after passing an ultra-filter. A. A. ELDRIDGE.

Centrifuging alkaline solutions of polonium. (MILES.) C. CHAMIÉ and A. KORVEZEE (Compt. rend., 1932, 194, 1488—1490; cf. A., 1931, 809, 1230; this vol., 236).—The max. proportions of Po centrifuged from solutions in NH₃ (3×10⁻⁴ to 10*N*) and aq.

NaOH (10^{-4} to $4N$) are 82% and 63%, respectively, for $0.1N$ and $0.007N$.
C. A. SILBERRAD.

Double refraction due to flow. P. BOEDER (Z. Physik, 1932, 75, 258—281).—The orientation of rod-like particles under forces due to Brownian motion and to shear has been examined in relation to the resulting double refraction. A. B. D. CASSIE.

Influence of non-electrolytes on the coagulation of gold hydrosol. H. TSUTSUI (J. Biochem. Japan, 1932, 15, 163—166).—EtOH, MeOH, camphor, thymol, Et urethane, and carbamide exert a sensitising action on the sol as indicated by the stability of the system towards NaCl. Glucose has no marked action, whilst Na glycocholate has a stabilising influence.

F. O. HOWITT.

Coagulation of colloids by electrolytes. XI. Cataphoretic and potentiometric measurements during coagulation of colloidal ferric hydroxide. A. J. RABINOVITSCH and E. FODIMAN (Z. physikal. Chem., 1932, 159, 403—413).—Potentiometric titration of $Fe(OH)_3$ sols with Na_2SO_4 and measurements of the rate of cataphoresis, v , in presence of varying amounts of Na_2SO_4 have shown that the superequiv. displacement of Cl^- by SO_4^{2-} (A., 1928, 586) does not run parallel with the variation of v , but is favoured by increase in the age of the sol; in some cases it may be absent. With increase in the Na_2SO_4 concn. v increases in all cases.
R. CUTHILL.

Influence of concentration of peptiser on velocity of coagulation of hydrosols of chromic and ferric hydroxides. J. LISIECKI (Rocz. Chem., 1932, 12, 241—257).—The velocity of coagulation of the above hydrosols by KCl depends on the concn. of peptising substances ($CrCl_3$ and $FeCl_3$).

R. TRUSZKOWSKI.

Photosensitising effect of colourless fluorescent substances on the flocculation of colloidal solutions. J. BOUCHARD (Compt. rend., 1932, 194, 1245—1246; cf. A., 1931, 907).—The action of ultraviolet light on a colloidal solution of As_2S_3 in presence of aesculin or β -naphthol- or β -naphthylamine-sulphonic acid reduces the period of flocculation by KCl from 75 to 60—35 min.
C. A. SILBERRAD.

Influence of various substances on the peptisation of ferric arsenate, phosphate, tungstate, and molybdate by ferric chloride. H. P. VARMA and S. PRAKASH (Z. anorg. Chem., 1932, 205, 241—250; cf. A., 1930, 1114).—Positive sols are obtained when Fe^{III} arsenate, phosphate, tungstate, or molybdate is peptised with aq. $FeCl_3$, the degree of peptisation decreasing in the order given. Peptisation is promoted by glycerol or glucose and repressed by carbamide or SO_4^{2-} . The relation between peptisation and gelatinisation, and the mechanism of the peptisation process, are discussed.
F. L. USHER.

Physico-chemical degradation of starch. R. HEINIGER (Kolloid-Beih., 1932, 35, 331—371).—The changes taking place in amyloamylose and amylopectin when boiled with H_2O have been followed by observing the sp. gr., p_H of the sol, reducing properties, surface tension, viscosity, adsorptive power, fluorescence, behaviour on ultrafiltration, and tenacity of

the paste. The results indicate an increase in the ultrafilterable portion at the expense of the colloidal material; this takes place mainly during the first 36 hr., and the concomitant changes in other properties have been examined. The change is due mainly to a physico-chemical disaggregation of the particles.

E. S. HEDGES.

Lyophilic colloids. XI. Electrolyte binding in albumin solutions. H. R. KRUYT and A. B. BOELMAN (Kolloid-Beih., 1932, 35, 165—202).—A method for accurate potential measurements in solutions of high electrical resistance is described and applied to the solutions of gelatin and albumin. The binding of Cl^- in the system albumin-NaCl could not be recognised; it is apparently masked by a hydration effect. In the systems gelatin- $AgNO_3$ and albumin- $AgNO_3$ the amount of bound Ag^+ varies exponentially with the equilibrium concn. Experiments with albumin sols of different concn. indicate that the binding of the ions is due to adsorption. The amount bound varies with the treatment of the gelatin and is decreased by any treatment which reduces the sp. surface. Isoelectric gelatin from which mineral matter has been removed by HCl binds more Ag^+ than does gelatin similarly treated with AcOH, but this is partly due to the formation of $AgCl$.

E. S. HEDGES.

Lyophilic colloids. XII. Character of electrical phenomena. H. R. KRUYT and H. G. B. DE JONG (Kolloid-Beih., 1932, 35, 203—210).—A discussion of the properties of the electrical double layer in hydrophobic and hydrophilic systems.

E. S. HEDGES.

Determination of the isoelectric point of gelatin. G. P. FAERMAN (J. Appl. Chem. Russ., 1931, 4, 321—323).—Shukov and Schukarev's method (A., 1925, ii, 386) is untrustworthy. Determination of the max. turbidity of the gel is preferred.

CHEMICAL ABSTRACTS.

Rhythmic phenomena in gels. J. M. JOHLIN (Science, 1932, 75, 462).—The pitch of the note which precedes the fracture of SiO_2 gels varies with time.

L. S. THEOBALD.

Influence of hydrolysed gelatin on the precipitation of silver chromate. B. N. DESAI and G. M. NABAR (Trans. Faraday Soc., 1932, 28, 449—452; cf. A., 1928, 126).—When approx. $0.01N$ - $AgNO_3$ is mixed with $0.01N$ - K_2CrO_4 in the presence of partly hydrolysed aq. gelatin the activity of Ag^+ , determined electrometrically, remains const. for a time and independent of the extent of hydrolysis, and then decreases rapidly to a const. val. The first appearance of red colour coincides with the commencement of the fall in the Ag^+ activity. This occurs earlier with more extensive hydrolysis and the final Ag^+ activity is higher. The results support the view that Ag_2CrO_4 is pptd. from true solution and not by coagulation of a colloidal sol, and that hydrolysis of gelatin does not facilitate pptn. by increasing free $[Ag^+]$.

J. G. A. GRIFFITHS.

Coacervation. R. S. T. MODDERMAN and L. W. J. HOLLEMAN (Nature, 1932, 129, 654).—Coacervation is discussed for the systems H_2O -gelatin-EtOH, H_2O -gelatin- Na_2SO_4 , and H_2O -gelatin-resorcinol.

L. S. THEOBALD.

Gels. III. Vapour pressure of silica gels. D. G. R. BONNELL (Trans. Faraday Soc., 1932, 28, 463—471; cf. this vol., 123).—Sorption isotherms of dialysed and undialysed SiO_2 gels were determined by a static method at 20°. During the first desorption the undialysed gels crumble spontaneously and remain thus during the reverse cycle until the v. p. of H_2O is approached, when the gels prepared with HCl , AcOH , and H_2SO_4 behave differently, but in all cases a clear liquid separates. With these gels the first sorption and desorption isotherms are not connected by part of the second desorption curve, but after the first cycle sorption and desorption of H_2O vapour become reversible. Other differences between undialysed and dialysed gels are noted and an explanation, based on Zsigmondy's theory, is suggested. Determinations of the vol. changes during desiccation support the conclusion that the H_2O sorbed by the gel is in the uncombined state. J. G. A. GRIFFITHS.

Dielectric constants of thixotropic systems and of oriented layers. H. KALLMANN and W. KREIDL (Z. physikal. Chem., 1932, 159, 322—335).—The dielectric const. of a thixotropic V_2O_5 sol measured with a wave-length of about 50 m. was about 7% greater than that of H_2O and diminished by about 6% when the gel was formed. From the smallness of the decrease it seems improbable that the H_2O mols. lose their freedom of motion to any considerable extent when the sol-gel transformation occurs. The decrease is ascribed to loss of the power of free rotation by the rod-shaped V_2O_5 particles. The dielectric const. of a thin layer of palmitic or lauric acid enclosed between parallel metal plates rises with diminution in thickness of the layer, attaining a limiting val. when the thickness is 10—20 μ . This effect, which is absent with a non-polar substance such as NHPh_2 , is ascribed to the presence of an oriented film of acid mols. on the surface of the layer. R. CUTHILL.

Primary dissociation constants of the methylcyclohexane-1:1-diacetic acids. Anomaly between the physical and chemical tests of the valency-deflexion hypothesis. D. J. G. IVES, R. P. LINSTAD, and H. L. RILEY (J.C.S., 1932, 1093—1100).—Conductometric measurements of cyclopentane-, cyclohexane-, 2-methylcyclohexane-, and 3-methylcyclohexane-1:1-diacetic acids give the following vals. for the primary dissociation const. $K_1 \times 10^4$ at 25°: 1.76, 3.23, 3.25, and 3.21, respectively. The results are discussed with reference to the valency-deflexion hypothesis. M. S. BURR.

Electrolytic dissociation of acids in salt solutions. IV. Dissociation constants of fatty acids with branched carbon chains, and activity relations of their ions in sodium chloride and potassium chloride solutions. V. Dissociation constants of aliphatic unsaturated acids, and activity relations of their ions in sodium and potassium chloride solutions. E. LARSSON (Z. physikal. Chem., 1932, 159, 306—314, 315—321; cf. this vol., 124).—IV. Extension of previous investigations to other fatty acids has shown that in NaCl and KCl solutions the vals. of $-\log \psi$ and $-\log \phi$ for a fatty acid are influenced only by the no. and nature of the atoms attached to the α -C atom and by branching of

the chain when that occurs at the α -C atom. The vals. for a mono- or tri-alkylacetic acid are practically independent of the constitution of the acid, and vary only with the nature and concn. of the salt which is present. For dialkylacetic acids the vals. at low salt concns. are little higher than for monoalkylacetic acids, but at high salt concns. the difference is greater.

V. Geometric isomerism caused by a C:C linking does not appreciably affect $-\log \phi$ and $-\log \psi$, and tetrolic acid has the same vals. as the crotonic acids. The vals. for an unsaturated acid at high salt concns. are always rather higher than for the corresponding saturated acid if the double linking is between the α - and β -C atoms. Introduction of an unsaturated C linking into a fatty acid affects the vals. only if it occupies the closest possible position to the CO_2H group. R. CUTHILL.

Extremely weak acids. J. B. CONANT and G. W. WHELAND (J. Amer. Chem. Soc., 1932, 54, 1212—1221).—The interaction of extremely weak acids, such as enols, alcohols, and derivatives of NH_3 and phenylated hydrocarbons, with the Na and K compounds of similar acids has been studied in anhyd. Et_2O . From the results, CPhMe_2 appears to be the weakest acid studied and BzMe the strongest; CPhCH , indene, and phenylfluorene are of nearly the same strength. A study of the interaction of $\text{C}_6\text{H}_4\text{Ph}\cdot\text{CPh}_2$ with CPh_3Na and of xanthane with $\text{C}_6\text{H}_4\text{Ph}\cdot\text{CPh}_2\text{Na}$ at several temp. showed no real parallelism between the rates and acid strength, since the K salt of the weakest acid reacts rapidly with the next four acids in the series. *Diphenyl-naphthylacetic acid*, m. p. 240°, its *Me* ester, m. p. 189—191°, *diphenyldiphenylacetic acid*, m. p. 220—222°, and its *Me* ester, m. p. 170°, have been prepared. C. J. WEST (c).

Acid hydrates and hydroxonium salts. A. HANTZSCH (Z. anorg. Chem., 1932, 205, 163—179).—A general exposition of the author's views regarding the constitution of acids in solution and as crystalline solids. F. L. USHER.

Buffer action of tungstate solutions. W. QVIST and A. LUND (Z. anorg. Chem., 1932, 205, 87—94).—The p_{H} of solutions of Na_2WO_4 has been studied with respect to the influence of concn., val. of the ratio $\text{WO}_3 : \text{Na}_2\text{O}$, and quantity of aq. HCl or H_2SO_4 added. Provided the ratio $\text{WO}_3 : \text{Na}_2\text{O}$ does not fall below 1, the p_{H} is very insensitive to the addition of acids, and the solutions can be used as buffers over the range p_{H} 7—8. F. L. USHER.

Activity coefficients of the silver ion in aqueous solutions of some strong electrolytes. II. J. B. CHLOUPEK and V. Z. DANEŠ (Coll. Czech. Chem. Comm., 1932, 4, 165—175).—E.m.f. measurements with saturated Ag_2SO_4 solutions containing variable amounts of K_2SO_4 or KNO_3 yield -0.7996 volt for the standard potential of Ag at 25°. The calc. activity coeffs. of the Ag and SO_4 ions are in fair agreement with the Debye-Hückel equation, assuming ionic diameters of 1 and 3 Å., respectively. H. F. GILBE.

Combinations of thoryl chloride and an alkali chloride. E. CHAUVENET and R. CHAUVENET

(Compt. rend., 1932, 194, 1246—1247).—The heat evolution on mixing solutions of ThOCl_2 and MCl ($\text{M} = \text{Li, Na, K, Rb, Cs, or NH}_4$) suggests the existence of compounds $\text{MCl} \cdot \text{ThOCl}_2$, except when $\text{M} = \text{NH}_4$. $\text{KCl} \cdot \text{ThOCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CsCl} \cdot \text{ThOCl}_2 \cdot 4\text{H}_2\text{O}$ were isolated in cryst. form. C. A. SILBERRAD.

Complex compounds of amino-acids with neutral salts. F. LEUTHARDT (Helv. Chim. Acta, 1932, 15, 540—557).—The depressing action of neutral salts (MgSO_4 , MgBr_2 , MgCl_2 , CaCl_2 , SrCl_2 , BaCl_2 , LiCl) on the p_{H} of solutions of NH_2 -acids (glycine, alanine, leucine, aspartic acid, asparagine, glycylglycine, and ovalbumin) has been determined by electrometric titration. MgCl_2 has no effect on the ultra-violet absorption spectrum (220—246 $\text{m}\mu$) of free glycine, but it weakens the absorption in the presence of alkali. The nature of the equilibria is considered in detail. D. R. DUNCAN.

Physico-chemical behaviour of polypeptides composed of *dl*-alanine. E. ABDERHALDEN and J. HEUMANN.—See this vol., 503.

Thermal dissociation of certain oxides and peroxides. IV. Calcium peroxide. M. BLUMENTHAL (Rocz. Chem., 1932, 12, 232—240).— CaO_2 exists in the difficultly dissociable α -form below 220° , and in the readily dissociable β -form above 220° . The temp. coeff. of dissociation of α - CaO_2 is 1.19.

R. TRUSZKOWSKI.

Thermodynamic activities in binary alloys. C. WAGNER and G. ENGELHARDT (Z. physikal. Chem., 1932, 159, 241—267).—From e.m.f. measurements with cells of the type molten alloy of metals 1 and 2 | molten salt of metal 1 | molten metal 1, the activity, a , of the baser constituent in the alloys Pb-Bi , Sn-Bi , Tl-Bi , Mg-Pb , and Ag-Au has been determined over a range of concns. and at either one or two temp., the results being on the whole in agreement with vals. calc. from existing data for distribution ratios and with data for heat of mixing. The variation of a with concn. agrees broadly with equations deduced by applying van der Waals' equation to binary mixtures, but Lorenz' method of finding the consts. in the equation of state must be used with care. The activities of Ag and Cu in solid alloys with Au have been determined at several temp., the measured potentials apparently being equilibrium vals.

R. CUTHILL.

Affinity of metals for sulphur. II. Thermal dissociation equilibria of sulphides of silver, copper, and arsenic. E. V. BRITZKE and A. F. KAPUSTINSKI (Z. anorg. Chem., 1932, 205, 95—112; cf. A., 1931, 169).—The thermal dissociation of Ag_2S has been examined at different temp. by measuring the partial pressure of H_2 in equilibrium with the solid phase. The dissociation pressure (of S_2) varies from 0.033 mm. at 912° to 0.456 mm. at 1067° . The dissociation of As_2S_2 and of As_2S_3 was determined by measuring the v.d., and of Cu_2S by a gas-streaming method. The pressure of S_2 in equilibrium with $\text{Cu}_2\text{S} + \text{Cu}$ at 1000° is about 10^{-10} atm. The following data are recorded: $2\text{As} + 2\text{S}$ (rhombic) = $\text{As}_2\text{S}_2 + 19.2$ kg.-cal., $2\text{Cu} + \text{S}$ (rhombic) = $\text{Cu}_2\text{S} + 20.2$ kg.-cal. Affinities for S : Cu^\dagger 45.49 kg.-cal. at 1004° , Ag 23.65 kg.-cal. at 1185° . F. L. USHER.

Vapour pressure of water over aqueous solutions of the chlorides of the alkaline-earth metals. IV. Evaluation of activity coefficients. J. R. I. HEBURN (J.C.S., 1932, 1284—1292).—The activity coeffs. calc. from v.-p. data at 25° for Ca , Sr , and Ba chlorides in H_2O are in general agreement with those derived from e.m.f. data, passing through min. vals. at approx. the same concn. The results also confirm to a certain extent Allmand's conclusions (A., 1927, 1029) relating to the connexion between v.-p. lowering and activity coeffs. M. S. BURR.

Binary systems: nitrates of metals of group II and water. I. Magnesium nitrate-water. A. SIEVERTS and W. PETZOLD (Z. anorg. Chem., 1932, 205, 113—126).—Solubility data for the above system have been determined. The stable cryohydric temp. is -31.5° . The enneahydrate is stable below -17.1° . The hexahydrate has congruent m. p. 89.3° , and forms a eutectic mixture with the dihydrate at 55.6° . The anhyd. salt (above 128°) could not be obtained owing to decomp. Isothermal dehydration curves and cooling curves establish the existence of a metastable tetrahydrate. F. L. USHER.

Sodium sulphate. T. OKUNO and K. MIYAZAKI (J. Soc. Chem. Ind. Japan, 1932, 35, 97—99B).—The solid phases in the system $\text{Na}_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ at 25° are Na_2SO_4 , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{Na}_3\text{H}(\text{SO}_4)_2$, $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$, NaHSO_4 , and $\text{NaH}_3(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. The dissociation pressures of NaHSO_4 and $\text{Na}_3\text{H}(\text{SO}_4)_2$ have been measured by means of Wöhler's apparatus and with a thermobalance. The velocity of decomp. of NaHSO_4 between 200° and 900° has been followed and changes in constitution during heating observed by X-ray analysis. J. W. SMITH.

Thermodynamic study of potassium hydr-oxide. F. L. E. SHIBATA, S. ODA, and S. FURUKAWA (J. Sci. Hiroshima Univ., 1932, A, 2, 85—102).— KOH forms three hydrates, $\text{KOH} \cdot 2\text{H}_2\text{O}$, stable below 27.3° , $\text{KOH} \cdot 1\frac{1}{2}\text{H}_2\text{O}$, stable below 33.4° , and $\text{KOH} \cdot \text{H}_2\text{O}$. The dissociation pressures and free energies of hydration are recorded, and the free energy of formation and entropy of KOH at 25° are found to be $-92,950$ g.-cal. and 23.0 , respectively.

C. W. DAVIES.

Thermodynamic study of sodium hydroxide. F. L. E. SHIBATA (J. Sci. Hiroshima Univ., 1931, A, 1, 215—228).—Measurements at 25° of the v. p. of NaOH and its saturated solution, and e.m.f. of the cell $\text{Na-Hg}|\text{NaOH} \cdot \text{H}_2\text{O}$ sat., $\text{HgO}|\text{Hg}$ lead to: (1) $\text{NaOH} + \text{H}_2\text{O} = \text{NaOH} \cdot \text{H}_2\text{O}$; $\Delta F = -2835$, $\Delta H = -2900$ g.-cal. (2) $\text{H}_2\text{O} + 0.9496\text{NaOH} \cdot \text{H}_2\text{O} = \text{NaOH}$ sat.; $\Delta F = -1556$, $\Delta H = +633$ g.-cal. (3) $\text{Na} + \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{NaOH}$; $\Delta F = -90,762$, $\Delta H = -102,401$ g.-cal. (4) The entropy of NaOH is 12.43.

C. W. DAVIES.

Decomposition pressures of crystalline hydr-oxides [with special reference to those] of aluminium and beryllium. R. FRICKE and H. SEVERIN (Z. anorg. Chem., 1932, 205, 287—308).—Isobaric (100 mm.) dehydration of cryst. diaspore, böhmite (bauxite), bayerite, hydrargillite, and stable and metastable $\text{Be}(\text{OH})_2$ has been carried out in vessels having a very small vol. (<1 c.c.). Although the materials were finely ground, the attainment of equi-

librium required from 1 to 10 weeks. In all cases the observed temp. of decomp. were considerably lower than those given by other workers. X-Ray examination affords evidence that the lattice of all these substances is built up from metal and hydroxyl ions, and dehydration must therefore be preceded by formation of H_2O . The thermal effect calc. from the temp. coeff. of dehydration represents chiefly heat of activation. The following vals. of d^{20} are given: böhmite 3.014, bayerite 2.529, hydrargillite 2.424, metastable $Be(OH)_2$ 1.920, stable $Be(OH)_2$ 1.924.

F. L. USHER.

Thermal analysis of the system lithium nitrate-thallos nitrate. H. V. A. BRISCOE, C. EVANS, and P. L. ROBINSON (J.C.S., 1932, 1100—1103).—The equilibrium diagram for $LiNO_3$ - $TiNO_3$ is simple and similar to that of $NaNO_3$ - $TiNO_3$. There is no evidence of compound formation or solid solution between 50° and 250° . The single eutectic at 136.5° corresponds with 63.8 mol.-% $TiNO_3$. The following consts. were redetermined and differ appreciably in some cases from earlier data: m. p. $LiNO_3$, $252.0 \pm 0.2^\circ$; m. p. $TiNO_3$, $206.0 \pm 0.2^\circ$; transition $\alpha \rightarrow \beta$ - $TiNO_3$, 143.5° ; $\beta \rightarrow \gamma$, 61.0° .

M. S. BURR.

System aniline, ethylaniline, and diethylaniline. T. YAGINUMA and K. HAYAKAWA (J. Soc. Chem. Ind. Japan, 1932, 35, 117—118B).—Phase diagrams are given for the systems NH_2Ph - $NHPhEt$, NH_2Ph - $NPhEt_2$, $NHPhEt$ - $NPhEt_2$, and NH_2Ph - $NHPhEt$ - $NPhEt_2$.

J. W. SMITH.

Thermodynamic study of the system iron-carbon-oxygen. II. H. DÜNWALD and C. WAGNER (Z. anorg. Chem., 1932, 205, 205—208; cf. A., 1931, 1128).—Polemical against Krings (this vol., 22).

F. L. USHER.

System calcium-sulphur-oxygen. J. ZAWADSKI (Z. anorg. Chem., 1932, 205, 180—192; cf. A., 1928, 1095).—Equilibrium pressures over $CaSO_4$ + CaO have been measured at and above 840° . The observed pressures decrease with time and reach a const. val. characteristic of anhydrite. The heat of reaction calc. from these data agrees with the accepted thermochemical val. A qual. and quant. study of the reactions $(4CaSO_3) CaS + 3CaSO_4 = 4CaO + 4SO_2$ and $CaS + 2SO_2 = CaSO_4 + S_2$ has also been made.

F. L. USHER.

Synthesis of calcium silicates. IV. S. NAGAI and K. AKIYAMA (J. Soc. Chem. Ind. Japan, 1932, 35, 118—122B; cf. this vol., 350, 481).—The systems CaO - SiO_2 - Fe_2O_3 , CaO - SiO_2 - Al_2O_3 , CaO - SiO_2 - Fe_2O_3 - Al_2O_3 have been studied at 1450° .

J. W. SMITH.

System CaO - Na_2O - Al_2O_3 . L. T. BROWN-MILLER and R. H. BOGUE (Bur. Stand. J. Res., 1932, 8, 289—307).—The system contains two ternary compounds, $3CaO, 2Na_2O, 5Al_2O_3$, m. p. $>1630^\circ$, and $8CaO, Na_2O, 3Al_2O_3$ dissociating at 1508° into CaO and liquid. The first compound forms eutectics with $3CaO, 5Al_2O_3$ (CaO 23, Na_2O 8, Al_2O_3 69%, 1550°), CaO, Al_2O_3 (CaO 30.5, Na_2O 5, Al_2O_3 64.5%, 1515°), $5CaO, 3Al_2O_3$ (CaO 40, Na_2O 4.5, Al_2O_3 55.5% 1450°), and the second ternary compound (CaO 43.2, Na_2O 10.3, Al_2O_3 46.5%, 1465°). CaO and $Na_2Al_2O_4$ form a eutectic with 20% CaO at 1565° .

Ternary eutectics are formed between $3CaO, 5Al_2O_3$, CaO, Al_2O_3 , and $3CaO, 2Na_2O, 5Al_2O_3$ (CaO 27.5, Na_2O 6, Al_2O_3 66.5%, 1465°), CaO, Al_2O_3 , $5CaO, 3Al_2O_3$, and $3CaO, 2Na_2O, 5Al_2O_3$ (CaO 38, Na_2O 4, Al_2O_3 58%, 1430°), and $5CaO, 3Al_2O_3$, $8CaO, Na_2O, 3Al_2O_3$, and $3CaO, 2Na_2O, 5Al_2O_3$ (CaO 46, Na_2O 5, Al_2O_3 49%, 1420°). Two quadruple points occur with CaO - $3CaO, Al_2O_3$ (57% CaO , 1535°) and with CaO - $8CaO, Na_2O, 3Al_2O_3$ (CaO 46.8, Na_2O 9, Al_2O_3 44.2%, 1508°), and three quintuple points between the 5:3 and 3:1 Ca aluminates and the 8:1:3 ternary compound (CaO 46.5, Na_2O 4.5, Al_2O_3 49%, 1423°), CaO , 3:1 Ca aluminate, and the 8:1:3 compound (CaO 50, Na_2O 6, Al_2O_3 44%, 1490°) and CaO , $Na_2Al_2O_4$, and the 8:1:3 and 3:2:5 ternary compounds (CaO 42.5, Na_2O 13, Al_2O_3 44.5%, 1475°). A. R. POWELL.

Phase equilibria in the system SiO_2 - ZnO - Al_2O_3 . E. N. BUNTING (Bur. Stand. J. Res., 1932, 8, 279—287).—In the binary system ZnO - Al_2O_3 the compound ZnO, Al_2O_3 (m. p. $1950 \pm 10^\circ$) forms a eutectic with ZnO at 83 mol.-% ZnO and $1720 \pm 10^\circ$. Tridymite, Zn_2SiO_4 , and $ZnAl_2O_4$ form a eutectic at $1305 \pm 5^\circ$ and SiO_2 52, ZnO 40, and Al_2O_3 8 mol.-%; ZnO , Zn_2SiO_4 , and $ZnAl_2O_4$ form a second eutectic in the ternary system at $1440 \pm 5^\circ$ and SiO_2 18.5, ZnO 71.3, and Al_2O_3 10.3 mol.-%. The system also contains two quintuple points which are not eutectics, one at $1400 \pm 5^\circ$ and SiO_2 63, ZnO 26, Al_2O_3 11 mol.-% with tridymite, $ZnAl_2O_4$, and mullite as the solid phases, and the other at about 1750° and about SiO_2 40, ZnO 23, and Al_2O_3 37 mol.-% with Al_2O_3 , $ZnAl_2O_4$, and mullite as the solid phases. The results are discussed with reference to a suitable refractory for retorts for the distillation of Zn ; it would appear that a high- Al_2O_3 mixture, in the neighbourhood of a mullite composition, should have a long life not only on account of its resistance to the slagging action of ZnO , but also because of its high resistance to spalling on rapid changes of temp. A. R. POWELL.

Heterogeneous equilibrium in the system $CdBr_2$ - KBr - H_2O . H. HERING (Compt. rend., 1932, 194, 1348—1350).— $CdBr_2$ crystallises with $4H_2O$ below, anhyd. above, 35° (cf. A., 1905, ii, 375). $KBr, CdBr_2$ crystallises from H_2O above 57.3° , but is decomposed by H_2O above 102° and on fusion; $KBr, CdBr_2, H_2O$, stable -9.3° to 57.3° , solubility congruent; $KBr, 2CdBr_2, H_2O$, exists 52 — 86° , never congruent; $KBr, 3CdBr_2, 4H_2O$, exists 14.8 — 57.5° , congruent 24 — 48° . $2KBr, CdBr_2$ was not obtained (cf. A., 1926, 791).

C. A. SILBERRAD.

Thermal analysis of ternary mixtures of isomeric compounds. T. VAN DER LINDEN (Helv. Chim. Acta, 1932, 15, 591—592).—Wyler's m. p. method for the analysis of mixtures of dinitrobenzenes (this vol., 259) is unsound. The author's method (A., 1913, ii, 106; cf. Kohman and Andrews, A., 1925, ii, 1053) is recommended. D. R. DUNCAN.

Formation and properties of precipitates. Theory of coprecipitation. I. M. KOLTHOFF (Chem. Weekblad, 1932, 29, 286—291).—Simultaneous pptn. may be due to (a) adsorption of foreign ions during crystal growth, causing irregular crystal formation, (b) surface adsorption after formation, (c) formation

of mixed crystals, and (d) chemical combination. Subsequent pptn., as in the case of MgC_2O_4 and CaC_2O_4 , and ZnS and CuS , is to be distinguished.

S. I. LEVY.

Heats of formation of rhenium oxides. W. A. ROTH and G. BECKER (Z. physikal. Chem., 1932, 159, 415—416; cf. this vol., 469).—Corrected heats of formation are Re_2O_7 , 297.5 ± 2 and ReO_3 , $82.5 \pm 10\%$ kg.-cal.

R. CUTHILL.

Heat of formation of compounds between lanthanum and magnesium and between lanthanum and aluminium. G. CANNERI and A. ROSSI (Gazzetta, 1932, 62, 202—211).—The heats of dissolution of Mg, Al, and La in HCl (1 mol./8.808 mols. H_2O) are 112.8, 125.4, and 172.4 kg.-cal. per g.-atom, respectively; the values for $LaMg$, $LaMg_3$, $LaAl_2$, and $LaAl_4$ are 279.5, 497.9, 387.1, and 631.8 kg.-cal. per mol., respectively. From these vals. the heats of formation of the four compounds are 5.7, 12.9, 36.1, and 42.2 kg.-cal. per mol., respectively.

O. J. WALKER.

Energy differences of different modifications of crystalline beryllium and aluminium hydroxides and heats of formation of crystalline zinc and beryllium hydroxides. R. FRICKE and B. WULLHORST (Z. anorg. Chem., 1932, 205, 127—144).—The heats of formation of cryst. Zn and Be hydroxides from oxide and H_2O have been calc. from heats of dissolution of the respective substances in aq. HF. The vals. found are: (BeO, H_2O) 1.87—3.35, (ZnO, H_2O) 2.28—3.21 kg.-cal., the val. in each case depending on the character of the oxide and hydroxide used. The energy differences observed indicate an order of stability in agreement with that given by measurements of solubility and v. p.

F. L. USHER.

Electrolytic water transport in barium chloride solution. J. BABOROVSKÝ and O. VIKTORIN (Coll. Czech. Chem. Comm., 1932, 4, 155—164).—The transport nos. of the Ba ion, and the electrolytic transport of H_2O in 0.1—2.0N-BaCl₂ solutions have been determined. Transference is towards the anode at concns. above about 0.2N, and in the reverse direction at lower concns. The quantity of H_2O transferred is a linear function of the dilution.

H. F. GILLBE.

Conductivity of nitric and perchloric acids, and the mobility of the hydrogen ion. M. HŁASKO and W. KLIMOWSKI (Rocz. Chem., 1932, 12, 201—212).—The conductivity coeffs. for HNO_3 and $HClO_4$, in concn. $< N/32$, are identical, and are 1% lower than the vals. calc. from Onsager's formula (cf. A., 1927, 517). The limiting mobility of H^+ is 355.1 and 355.0 for the two acids at 25°.

R. TRUSZKOWSKI.

Electrical conductivity of binary aggregates. G. S. SON FREY (Z. Elektrochem., 1932, 38, 260—274).—Theoretical. Lichtenecker's equation (cf. A., 1925, ii, 632) is inapplicable for high ratios of the conductivities of the two components. Formulæ are derived for different types of binary aggregates for ratios between 1 and ∞ . The calc. relation between composition and conductivity agrees closely with the observed vals. both for alloys and for systems composed of insulating and conducting materials, such as,

e.g., sand saturated with a solution of an electrolyte. The great influence of a poorly conducting metal (e.g., Bi or Pb) on the conductivity of another metal (Ag or Mg), which in some cases has been attributed to mixed crystal formation, is shown to be in accordance with the theory. Application of the formulæ to the correction of observed conductivities of substances containing impurities is described.

H. F. GILLBE.

Behaviour of quartz electrodes. II. B. VON LENGYEL and T. MÁTRAI (Z. physikal. Chem., 1932, 159, 393—402; cf. this vol., 471).—Measurements with quartz electrodes in acid-alkali cells show that the electrode potential passes through a min. in about 1N-acid, then rises and passes through a max. in about 0.01N-alkali. The quartz electrode probably represents a limiting type of glass electrode. Its potential is determined by adsorption effects, whereas the potential of a soft glass electrode is influenced by distribution and diffusion.

R. CUTHILL.

Electrometric titration and certain properties of ferrous sulphate. N. A. SCHISCHAKOV (J. Gen. Chem. Russ., 1931, 1, 1012—1025).—The E_h of a solution containing Fe^{2+} and Fe^{3+} is given by $E_h = 0.380 + 0.058 \log c_3/c_2$, where c_2 and c_3 are the concn. of Fe^{2+} and Fe^{3+} , respectively. Fe^{2+} can be determined potentiometrically by titration with $K_2Cr_2O_7$, the break in the curve obtained being the more marked the greater is the concn. of acid present. $FeSO_4$ does not undergo oxidation in the presence of atm. O_2 when its concn. is $> 0.001M$; at higher concn. the velocity of oxidation is proportional to the concn., and is greater in presence of light. The reaction is catalysed by smooth Pt, and more powerfully by platinised Pt. The concn. of Fe^{2+} can be found from the E_h found for solutions for which the ratio c_3/c_2 varies from 5/95 to 95/5, using a rotating Pt electrode for determination of E_h , and extrapolating from the E_h - $K_2Cr_2O_7$ curve.

R. TRUSZKOWSKI.

Electrochemical periodicities. J. A. V. BUTLER and G. ARMSTRONG (Nature, 1932, 129, 613—614).—Marked periodicities occur at small c.d. in the anodic polarisation of Pt electrodes in dil. H_2SO_4 saturated with H_2 . The periodicities are not obtained during the first anodic polarisation of the electrode. A mechanism in which the electrons passing into the metal are derived from absorbed H_2 is discussed.

L. S. THEOBALD.

Reduction of aromatic mono- and poly-nitro-compounds. XIII. K. BRAND and F. STRACHE (J. pr. Chem., 1932, [ii], 133, 355—364; cf. A., 1931, 1151).—When $PhNO_2$ is reduced with Zn dust and $CaCl_2$ for 5 min., the solution after filtration and extraction with Et_2O has p_H 11.75. When reduction is continued for 40 min., the p_H is 11.05, rising after 40 min. to 11.3. When NH_4Cl is used instead of $CaCl_2$ and reduction continued for 40 min., the p_H is 7.9 (max. after 40 min., falling after 60 min. to 7.6); these lower vals. are due to loss of NH_3 during reduction and in the stream of H_2 during the potentiometric measurements. The mechanism of the reduction previously proposed (A., 1928, 1366) is proved experimentally. The alkalinity of the solution is

due to the formation of $Zn(OH)_2$. Extraction of aq. $NaOAc$ with Et_2O has no effect on its p_H .

R. S. CAHN.

Time factor in anodic passivation of metals. W. J. MÜLLER (Trans. Faraday Soc., 1932, 28, 471—473).—Polemical against Shutt and Stirrup (cf. A., 1930, 1527). Vigorous stirring does not necessarily prevent the formation of salt or surface layers at the anode. The observations of Shutt and Stirrup are consistent with the existence of a surface layer.

J. G. A. GRIFFITHS.

Specific nature of energy exchange in uni-molecular reactions. E. W. R. STEACIE (J. Amer. Chem. Soc., 1932, 54, 1695).— Me_2O and Et_2O decompose in an almost identical way; they have a pronounced resemblance in physical properties and in the manner in which the velocity coeff. decreases with pressure, yet have no activating effect on each other.

C. J. WEST (c).

Chemical kinetics of De Donder and Arrhenius' heat of activation. P. VAN RYSSELBERGHE (Bull. Acad. roy. Belg., 1932, [v], 18, 170—179).—Mathematical. A relation between chemical affinity and heat of activation is deduced, and considered in relation to high temp., complete reactions, and photo-chemical reactions.

N. M. BLYTH.

Kinetics of degradation of long-chain molecules. F. KLAGES (Z. physikal. Chem., 1932, 159, 357—367).—The kinetics of the degradation are worked out theoretically assuming that the velocity coeff. of decomp. is the same for all the linkings in the chain but one. The results agree with existing experimental data (A., 1930, 1025).

R. CUTHILL.

Kinetics of degradation of long-chain molecules. W. KUHN (Z. physikal. Chem., 1932, 159, 368—373).—The kinetics are worked out on the lines followed by Klages (cf. preceding abstract), but in a more exact manner.

R. CUTHILL.

Inflammation of mixtures of hydrogen and oxygen by hydrogen atoms. F. HABER and F. OPPENHEIMER (Z. physikal. Chem., 1932, B, 16, 443—459).—Explosion already occurs at about 300° when H_2 containing about 10⁻⁴% H atoms is mixed with O_2 under 20—150 mm. The H atoms are the cause of explosion, above 80 mm. at any rate, for the ignition temp. of the mixtures without at. H on quartz lie above 500°. Increase in pressure is unfavourable to surface ignition, but promotes the explosive reaction, possibly because the H atom concn. was increased.

R. CUTHILL.

Chemical kinetics in a vessel surrounded by a large thickness of mercury. M. BOLL (Compt. rend., 1932, 194, 1242—1243).—Using the author's electrometric method (cf. A., 1912, ii, 384) the velocity coeff. of the hydrolysis of $H_2PtCl_2(OH)_2$, in a tube of diam. 2 cm. placed vertically in a vessel of 20 cm. diam., filled with Hg, was 0.002 c.g.s., compared with 0.0130 when Hg was absent (cf. A., 1919, ii, 256). It is suggested that the difference is due to cosmic rays. No such difference was observed in the inversion of sucrose.

C. A. SILBERRAD.

Deterioration of hypochlorites. R. H. AGUILAR.—See B., 1932, 382.

Rate of hydrolysis of pyrophosphoric acid. J. MUUS (Z. physikal. Chem., 1932, 159, 268—276; cf. A., 1927, 26).—The hydrolysis in $N-KCl$ at various $[H^+]$ at 20° and 40° is kinetically unimol., the velocity coeff. being proportional to $[H^+]$. The reaction apparently consists in the hydrolysis of $H_3P_2O_7$ catalysed by H^+ . From H electrode measurements the second and third dissociation consts. of $H_4P_2O_7$ are found to be 2.7×10^{-2} and 3×10^{-6} , respectively, in the reaction medium.

R. CUTHILL.

Oxidation of sodium sulphide and sodium hydrogen sulphide. S. A. SCHUKAREV and E. M. KIREEVA-TUZULACHOVA (J. Gen. Chem. Russ., 1931, 1, 1125—1144).—The products of oxidation of aq. $NaHS$ or Na_2S by atm. O_2 are Na_2SO_3 , $Na_2S_2O_3$, and Na_2SO_4 ; those of $Na_2S_2O_3$ are S , Na_2SO_3 , and Na_2SO_4 . The reaction of oxidation of $NaHS$ is one of zero order. The velocity of oxidation of Na_2SO_3 is reduced by the presence of $Na_2S_2O_3$, which, however, itself undergoes oxidation in the presence of Na_2SO_3 . The velocity of oxidation of HS' falls with increase in p_H and with increasing concn. of $NaHS$ or Na_2S . The reaction is represented as $HS' \longrightarrow HSO_2' \longrightarrow (a)S_2O_2''$, $(b)HSO_3' \longrightarrow HSO_4'$.

R. TRUSZKOWSKI.

Chemical reactions in concentrated electrolytes. Reduction of vanadic acid by hydrogen bromide and its course in concentrated electrolyte. (In sulphuric acid with constant evolution of bromine.) I. M. BOBTELSKI and S. CZOSNEK (Z. anorg. Chem., 1932, 205, 401—413).—In conc. H_2SO_4 the rate of reduction of V^V to V^{IV} by HBr is directly proportional to the concn. of V^V , but is proportional to the HBr concn. only in a dil. solution of the latter. For const. HBr and V^V , but increasing concn. of H_2SO_4 , no reaction takes place until there are less than 12 mols. of H_2O to 1 mol. of H_2SO_4 . For 10—5 H_2O the reaction velocity is inversely proportional to H_2O . Below 4 H_2O the results are uncertain and only slightly influenced by the amount of H_2O . The influence of increasing HBr depends on the concn. of H_2SO_4 and under certain conditions an optimum concn. of HBr is obtained. The position of this is not changed by temp., but the max. becomes more marked with rising temp.

If the Br formed is not removed the reaction ceases. HCl behaves similarly to H_2SO_4 . If different salt solutions are added to a mixture containing less than the optimum concn. of HBr a definite neutral salt effect is observed and the reaction is considerably accelerated, but there is practically no salt effect above the optimum concn. of HBr . The reverse is the case for Zn salts.

M. S. BURR.

Equilibria and rates of some organic reactions. J. B. CONANT (Ind. Eng. Chem., 1932, 24, 466—472).—The relation between the structure of compounds and the free energy of reaction in the standard states is discussed with reference to the reduction of quinones and the recently investigated equilibria between the keto and enol isomerides of substituted acetoacetic esters in the gas phase. The free energy of enolisation has been calc. and the results for the vapours are closely parallel to those obtained with dil. solutions in C_6H_{14} . The disturbing influence of solvents on many equilibria is emphasised. Reactions are dis-

cussed in which close relationships exist between rates of reaction and equilibria (cf. A., 1930, 322, 711). The rate of formation of the semicarbazones of pyruvic acid, four aldehydes, and three ketones has been investigated in buffer solutions. The reaction takes place between free semicarbazide and the carbonyl compound and is catalysed by acids, but at acidities $> p_H$ 4.9 the acceleration is opposed by a decrease in the concn. of free semicarbazide owing to salt formation. There is no apparent relation between the velocity of formation and the stability of the semicarbazide as measured by the hydrolysis const., but there appears to be a fairly simple relation between structure and the energy relationships of semicarbazone formation, the equilibrium const. being determined by factors similar to those governing the dissociation consts. of acids. J. G. A. GRIFFITHS.

Oxidation velocity of sodium sulphate solution by oxygen in presence of a molecular film of fatty acid. S. MIYAMOTO, T. KAYA, and A. NAKATA (J. Sci. Hiroshima Univ., 1931, A, 1, 203—214).—The max. rate of absorption of O_2 by a Na_2SO_3 solution which is rapidly stirred without breaking the surface is unaffected by addition of stearic acid. This disproves the existence under these conditions of a stationary surface film through which the O_2 must diffuse. C. W. DAVIES.

Influence of certain agents on the velocity of formation and thermal decomposition of some carbonates. J. ZAWADZKI and S. BRETZNAJDER (Compt. rend., 1932, 194, 1160—1162).—The velocity of absorption of CO_2 by CaO or CdO is not in accordance with the equation $v=K(p-P)$, where K is a const., p the actual and P the equilibrium pressure, but increases at first more rapidly, passes through a max., and then declines. Occasionally the reaction stops half completed, but continues after a period of rest. C. A. SILBERRAD.

Carbon dioxide absorption velocity of potassium and sodium hydroxide solutions. K. MASAKI (J. Biochem., Japan, 1932, 15, 29—32).—Following a reconsideration of the data previously obtained (A., 1931, 916) the corrected interpretation is that the CO_2 absorption velocity of $N-KOH$ is 1.14 times that of $N-NaOH$ at any temp. between 11° and 25° . F. O. HOWITT.

Reactions between carbon and certain gases. W. E. J. BROOM and M. W. TRAVERS (Proc. Roy. Soc., 1932, A, 135, 512—537).—Measurements have been made of the ratio $K_t=P_{CO}/P_{CO_2}$, and of the rates of reaction of sugar C and coconut C with CO and CO_2 . The influence of the H_2 present in the C and the presence of O_2 retained on the C on the rate of reduction of CO_2 has been investigated. The reaction between C, CO , and CO_2 is not represented by $C+CO_2=2CO$, but takes place in two stages: $CO_2+C=CO$ gas + C-O complex and $CO+C=C-CO$ complex. L. L. BIRUMSHAW.

Reduction of cupric oxide by carbon monoxide and hydrogen. A. JULIARD (Bull. Soc. chim. Belg., 1932, 41, 65—84).—A detailed description of an experimental method used to measure the rate of

reduction of CuO by CO or H_2 is given. Results obtained by it are satisfactorily reproducible. F. L. USHER.

Reduction of cupric oxide by carbon monoxide and hydrogen. A. JULIARD (Bull. Soc. chim. Belg., 1932, 41, 138—151; cf. preceding abstract).—The influence of the vol. and thermal treatment of CuO , the velocity and concn. of CO , and the temp. of reaction ($450-900^\circ$) has been studied. The velocity of reaction depends largely on factors affecting the porosity of the reduced Cu . E. S. HEDGES.

Temperature increment of the velocity of heterogeneous reactions. II. Reduction of silver halides. K. FISCHBECK and K. SCHNAIDT (Z. Elektrochem., 1932, 38, 299—304).—The reduction of $AgCl$ by H_2 proceeds without an induction period, and its velocity at const. temp. is determined only by the available $AgCl$ surface, i.e., diffusion is of no account. The following heats of activation, in $kg\text{-cal.}$, have been determined: $AgCl$ (fused) 61.0; $AgCl$ (pptd.) 20.7; $AgBr$ (pptd.) 22.5. H. F. GILLBE.

Intercrystalline corrosion of duralumin. A. J. SIDERY, K. G. LEWIS, and H. SUTTON.—See B., 1932, 429.

Distribution of corrosion. S. C. BRITTON and U. R. EVANS.—See B., 1932, 429.

Kinetics of a type of heterogeneous reactions. II. Mechanism of combustion of lump fuel. S. P. BURKE and T. E. W. SCHUMANN (Ind. Eng. Chem., 1932, 24, 451—453; cf. A., 1931, 574).—The authors' mathematical treatment is extended to the combustion of a sphere of solid fuel and the theory is confirmed, in general, by the work of Smith and Gudmundsen (B., 1931, 466). The rate of reaction increases with diminution of particle size and with increase of air velocity, but vals. of the surface temp. of C do not accord with the theory. The discrepancies may be related to the effects of H_2O and the formation of CO in the combustion process. J. G. A. GRIFFITHS.

Rôle of phosphate in oxidation processes. A. M. MALKOV and N. ZVETKOVA (Biochem. Z., 1932, 246, 191—202).—Phosphate inhibits the decomp. of H_2O_2 by $FeSO_4$ and also inhibits the oxidation of various sugars by the system $Fe^{II}+H_2O_2$. The oxidation of sugar by $FeSO_4$ is accelerated by 0.15M-phosphate, but is completely inhibited by higher concns. ($M/1-M/3$). P. W. CLUTTERBUCK.

Constitutional factors controlling prototropic changes in carbonyl compounds. II. Acid and base catalysis in the bromination of halogenated acetones. H. B. WATSON and E. D. YATES (J.C.S., 1932, 1207—1215).—Measurements of the rate of bromination of various halogenated acetones have confirmed the conclusion (cf. this vol., 129) that an electron-attracting substituent reduces the extent to which the ketone co-ordinates with an acid catalyst and increases the ease with which the proton ionises. The influence of the halogen substituent is shown by the change in the ratio k_{acid}/k_{base} , as expressed in the displacement of the point of min. velocity in the direction of higher acid concn. This displacement is

very marked and is continuous as halogen atoms are successively introduced into the mol. of COMe_2 .

E. S. HEDGES.

Catalysis by hydrogen chloride in the system acetic acid-ethyl alcohol-ethyl acetate. C. A. DURRUTY (Anal. Asoc. Quim. Argentina, 1931, 19, 227—253).—The equilibrium const. of the esterification is 3.7 at 100° . The net velocity of formation of AcOEt is proportional to the AcOH concn. An expression has been derived for the velocity of the reaction in presence of HCl ; at low HCl concns. the velocity is proportional to the concn., and, further, the equilibrium const. increases in an approx. linear manner with increase of the (initial) HCl concn. Equilibrium is attained within 80—90 hr., and the percentage of free HCl at equilibrium is 5—10% of that present initially.

H. F. GILLBE.

Activation of complex salts in aqueous solution. II. P. PFEIFFER and K. QUEHL (Ber., 1932, 65, [B], 560—565; cf. this vol., 30).—Increase in the concn. of the camphorsulphonic ion greatly enhances the activation of the $[\text{Zn phen}_3]^{++}$ ion (phen=phenanthroline). The activating effect of α -bromo- π -camphorsulphonic acid on ZnSO_4 and phenanthroline (1:1) is comparatively small. Activation of $[\text{Zn phen}_3]\text{SO}_4$ by cinchonine hydrochloride or quinine sulphate is not due to entry of the alkaloid into the Zn complex. Activation is caused by cinchonine mono- but not by di-methochloride. Nicotine is active. The salts $[\text{Cd } 1:1\text{-dipyridyl}_3]\text{X}_2$ and $[\text{Cd phen}_3]\text{X}_2$ in H_2O are similarly activated by optically active acid ions or optically active alkaloids. The compounds $[\text{Cd phen}_3](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $[\text{Cd phen}(\text{OH})_1](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are described.

H. WREN.

Catalysis in an inert solvent. E. A. MOELWYN-HUGHES (Nature, 1932, 129, 316).—For the mutarotation of Be benzoylcamphor in CCl_4 with $\text{C}_5\text{H}_5\text{N}$ or EtOH as catalysts the observed vals. agree with those calc. from Lewis' gas collision formula. This affords another example of a reaction proceeding in solution at the same rate as theory predicts for the gaseous phase (cf. Traill, this vol., 346). L. S. THEOBALD.

Effect of magnesium hydroxide on the oxidation of quinol. A. SAINT-MAXEN (Compt. rend., 1932, 194, 1583—1585).—The oxidation of quinol (cf. A., 1930, 1128) is not affected by a saturated aq. solution of $\text{Mg}(\text{OH})_2$ or by $\text{Mg}(\text{OH})_2$ pptd. in the hot. A freshly-prepared suspension of $\text{Mg}(\text{OH})_2$ activates the oxidation during 10 min.; in presence of 50% glycerol, the activity is retained for some days. Conductivity measurements indicate the existence of an equimol. compound of $\text{Mg}(\text{OH})_2$ and quinol. An aq. solution of the product obtained when hydrated $\text{Mg}(\text{OAc})_2$ is heated at $110^\circ/30$ mm. in N_2 also activates the oxidation; max. action is after about 24 hr., and the activity parallels the viscosity of the reaction mixture.

H. BURTON.

Mechanism of decomposition of esters in presence of feebly alkaline alcohol. E. M. BELLET (Compt. rend., 1932, 194, 1655—1658; cf. this vol., 42).—Displacement of PhOH from PhOAc by EtOH in presence of a little NaOH becomes less rapid as the solution becomes neutral, and is probably due to

addition to the C:O group, which is activated by alkali (or acid).

E. W. WIGNALL.

Desensitisers, antioxygens, and antifuorescents. E. BAUR (Z. physikal. Chem., 1932, B, 16, 465—470).—The variation with concn. of the effect of these substances may be expressed by $v=1/[\alpha+\beta(D)]$, where v is the ratio of the reaction velocity or intensity of fluorescence to that in absence of the added substance, D the concn. of the latter, and β a const. which is a measure of its effectiveness (cf. A., 1929, 892). It is therefore concluded that all three types of inhibition depend on a mol. electrolysis involving the inhibitor and the active mols. of the dark reaction or those created by light absorption (cf. A., 1928, 1338).

R. CUTHILL.

***o*-Quinones as enzyme models. III. Experiments in alkaline media.** B. KISCH and K. SCHUWIRTH (Biochem. Z., 1932, 247, 371—385; cf. this vol., 427).—The optimum reaction for the deamination of glycine (as measured by yield of NH_3) by pyrocatechol derivatives is between p_{H} 9 and 11 and is dependent on the nature of the catalysts, which themselves are affected, in differing degrees, by the reaction. In consequence of the action of O_2 on the catalysts the optimum lies the more to the alkaline side of neutrality the smaller is the amount of air present. The yield of NH_3 resulting from the action of hydroxyquinol may reach 70% of the theoretical. In the region p_{H} 6.0—12.0 serine is deaminated by the catalysts almost to the same extent as is glycine. Leucine is deaminated to a much smaller extent, whilst *iso*-leucine, valine, α - and β -aminopropionic acids and α -aminobutyric acid are not appreciably affected.

W. MCCARTNEY.

Catalysts for the production of hydrogen by means of the water-gas reaction. V. Thermal sensitivity of ferric oxide catalyst. VI. Thermal influence on the activity of ferric oxide-chromium sesquioxide catalysts. I. R. YOSHIMURA (J. Soc. Chem. Ind. Japan, 1932, 35, 85—87B, 87—88B; cf. A., 1931, 1017, 1134; this vol., 235).—V. Fe_2O_3 loses its catalytic effect for CO oxidation when heated in air above 700° . This coincides with the temp. at which a pastille of Fe_2O_3 shows a sharp vol. contraction when heated. There is no abrupt change in the velocity of reaction with SiO_2 at this temp., so it is concluded that there is no allotropic change although there is a magnetic transformation. The effect is attributed to the unsaturated atoms, to which the catalytic activity appears to be due, shifting from the crystal corners and angles to more stable configuration.

VI. The magnetic transformation point of Fe_2O_3 is lowered by addition of Cr_2O_3 , but not the temp. at which Fe_2O_3 pastilles contract abruptly.

J. W. SMITH.

Production of hydrogen sulphide by heating paraffin and other hydrocarbon mixtures with sulphur. E. D. SCUDDER and R. E. LYONS (Proc. Indiana Acad. Sci., 1931, 40, 185—188).—Lampblack and anhyd. AlCl_3 are effective catalysts.

CHEMICAL ABSTRACTS.

Sulphuric acid catalysis. V. B. NEUMANN [with K. KNOBLICH] (Z. Elektrochem., 1932, 38, 304—

311).—Catalysis of the reaction $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ by various oxides and by mixtures of CuO and Cr_2O_3 has been studied. CuO is active only at above 400° , CuSO_4 being the sole intermediate product; conversion is a max. (58.73%) at 700° . At temp. below that at which the dissociation pressure of CuSO_4 is considerable (650°) the catalyst is sluggish. The activity of MnO_2 rises to a max. (18.3%) at 560° , whilst that of the Mn_2O_3 then formed rises from about 12% at 600° to 22% at 700° ; Mn_3O_4 produces about the same percentage conversion as Mn_2O_3 . PbO_2 and Bi_2O_3 are scarcely active, owing to formation of sulphate. The reaction in presence of MoO_3 commences only at the temp. at which the catalyst begins to sublime (600°), and reaches a max. (47%) at 720° ; no apparent change takes place in the MoO_3 . UO_3 is inactive below 700° , when U_3O_8 is formed, but very little conversion takes place and UO_2SO_4 is produced. With CeO_2 13.67% conversion is obtained at 700° . A mixture of CuO with Cr_2O_3 (2 : 1) is slightly more active than is Cr_2O_3 alone, but a 1 : 1 mixture is less active; CuSO_4 is formed, and the activity in time approximates to that of Cr_2O_3 . H. F. GILLBE.

Platinum versus vanadium as catalyst for sulphuric acid. A. P. THOMPSON.—See B., 1932, 381.

Reduction of zinc oxide in presence of metallic copper. V. A. PLOTNIKOV and O. K. KUDRA (J. Gen. Chem. Russ., 1931, 1, 1075—1079).—When mixtures of CO and H_2 are passed over Cu-Zn catalyst at 400° , the particles of Cu become coated with brass, pointing to the formation of a volatile Zn compound, which decomposes on the surface of Cu . The process of synthesis of MeOH is hence explained as follows: $2n\text{ZnH}_2 + \text{Cu}(\text{CO})_n \rightarrow \text{Cu} + 2n\text{Zn} + n\text{MeOH}$.

R. TRUSZKOWSKI.

Oxidation of phosphorous acid by water in the presence of colloidal metals. A. A. VEDENSKI and A. V. FROST (J. Gen. Chem. Russ., 1931, 1, 1108—1113).—The oxidation of H_3PO_3 by H_2O is catalysed by colloidal Pt , Cu , or Ag . The catalysts are activated by H_3PO_4 in small concn., whilst at higher concn. they are inactivated. R. TRUSZKOWSKI.

Heterogeneous catalysis of binary gas reactions. C. KRÖGER (Z. anorg. Chem., 1932, 205, 369—397).—Heterogeneous catalysis of binary gas reactions may be physical, whereby the catalysed reaction takes place in an adsorbed layer, or chemical, when the surface of contact undergoes a permanent chemical alteration due to the formation of stable intermediate compounds. There are two kinds of chemical catalysis, the first in which a valency change takes place in the contact metal, and the second kind in which no valency change occurs. The factors determining the two different kinds of chemical catalysis are discussed with reference to particular cases. M. S. BURR.

Oxidation of ethyl alcohol by air in presence of binary or ternary catalysts. MARTINEAU (Compt. rend., 1932, 194, 1350—1353).— C-ZrO_2 and C-ThO_2 catalysts are prepared by treating with aq. NH_3 active C impregnated with the appropriate nitrate and drying at 150° . $\text{Cu-Ce}_2\text{O}_3$ and Cu-ThO_2 mixtures are

obtained by mixing Ce_2O_3 or ThO_2 with Cu carbonate, treating with NH_3 , and reducing with H_2 at 300° . Ternary catalysts, Cu-C-oxide , are prepared by a combination of these methods. The oxidation of EtOH by air at 63° in contact with these catalysts is measured; the max. efficiency is shown by 1C , 1Cu , 1ZrO_2 , and 10C , 2Cu , 1ThO_2 , the latter effecting oxidation at a measurable rate at $15-20^\circ$.

H. A. PIGGOTT.

Preparation of a catalyst (aluminium ethoxide) for the synthesis of ethyl acetate from acetaldehyde. K. SUMIYA, S. YAMADA, and Y. TAJIMA (J. Soc. Chem. Ind. Japan, 1932, 35, 88—91B).—The prep. of $\text{Al}(\text{OEt})_3$ by the action of EtOH on Al in AcOEt solution, using a mixture of I and HgCl_2 as catalyst, is accelerated by the addition of anhyd. FeCl_3 . The catalyst solution thus prepared enables AcOEt to be synthesised from MeCHO with very high yield.

J. W. SMITH.

Dehydration of phenol. Contact catalysis. E. BRINER, (MME.) J. BRON-STALET, and H. PAILLARD (Helv. Chim. Acta, 1932, 15, 619—634).—At 450° in the absence of a catalyst, PhOH is converted slowly but completely into Ph_2O and H_2O . The reaction occurs in the gas phase and is accelerated by increase of pressure. In presence of ThO_2 the reaction is much quicker, but is reversible, only 60—64% of the PhOH being decomposed at 450° , 54% at 500° , and 50.1% at 540° . Pressure has no influence on the velocity, the reaction occurring in an adsorbed phase. The heats of adsorption account for the difference in the equilibrium composition. Equilibrium was reached from both sides, and static and dynamic methods gave approx. the same results. The best catalyst was prepared by pptg. from boiling solutions of $\text{Th}(\text{NO}_3)_4$ and KOH and drying at 250° . With Al_2O_3 a similar equilibrium is established, max. dehydration (72—85%) occurring at 420° , but phenylene oxide is formed simultaneously. β -Naphthol at 450° decomposes completely to β -naphthyl oxide in the absence of a catalyst, whilst the % decomp. at equilibrium with ThO_2 is 58. The heat of combustion of Ph_2O is 1455 kg.-cal. D. R. DUNCAN.

Suitability of cobalt catalysts for benzene synthesis. F. FISCHER and H. KOCH.—See B., 1932, 376.

Use of nickel as a catalyst for hydrogenation. II. L. W. COVERT, R. CONNOR, and H. ADKINS (J. Amer. Chem. Soc., 1932, 54, 1651—1663; cf. A., 1931, 919).—The amount of Ni held by the support, the proportion of Ni compounds reducible to metal, and the optimum time and temp. for the reduction of Ni oxides to the active catalyst depend on the precipitants and mode of pptn. A method of preparing easily reproducible and very active catalysts is described. Various additional elements incorporated in the catalyst may increase its activity in respect of some hydrogenations and inhibit others. The course of certain hydrogenations is considerably affected by the presence of amino-compounds. The optimum conditions for the hydrogenation of various org. compounds have been established. C. J. WEST (c).

Alkali borides. L. ANDRIEUX and D. BARBETTI (Compt. rend., 1932, 194, 1573—1574; cf. this

vol., 348).—130 g. of $\text{Na}_4\text{B}_2\text{O}_7$ and 30 g. of NaF with varying amounts of CaO (4–12 g.), SrO (5–10 g.), BaO (50–60 g.), CeO_2 (3–20 g.), La_2O_3 (15 g.), Nd_2O_3 (10–12 g.), or ThO_2 (4–15 g.) were electrolysed at 950° . Black crystals of $x\text{MB}_6\cdot y\text{NaB}_6$ ($M=\text{Ca}$, etc.) were obtained. x decreases as the amount of added oxide is less, but below a certain limit, e.g., about 50% for ThB_6 , the mixture is unstable and some impure B is formed. Similar results were obtained with K and Li. C. A. SILBERRAD.

Metallic lanthanum free from iron and silicon. F. TROMBE (Compt. rend., 1932, 194, 1653–1655; cf. A., 1931, 1253).—With the arrangement described for Ce a mixture of LaCl_3 60 parts, KCl 35, and CaF_2 5, electrolysed at 960 – 980° with a current of 12 amp. per 25 g. of LaCl_3 at 7 volts (c.d. 4 amp. per sq. cm.), yields 65% La, free from Ca or Al, and containing 0.005–0.1% Fe, and, if prepared in a fluorite crucible, <0.05% Si; m. p. $885\pm 5^\circ$, Brinell hardness 36, d 6.139. C. A. SILBERRAD.

Preparation of potassium ferricyanide by electrolytic oxidation of potassium ferrocyanide in aqueous solution. (a) V. F. JUFEREV and J. I. BOKINIK, (b) V. F. JUFEREV and L. L. KUGMIN (Bull. Inst. polytech. Ivanovo-Vosniesensk, 1930, 15, 163–179, 181–196).—(a) Grube's results (A., 1914, i, 814) are confirmed; efficient stirring is necessary. The fine crystals (yield 40%) contain 0.1–0.3% of $\text{K}_4\text{Fe}(\text{CN})_6$, larger crystals contain 0.5%, and the mother-liquor 1–1.5%. Recrystallisation was effected with simultaneous oxidation with KMnO_4 in presence of AcOH . Evaporation after oxidation results in decomp. of $\text{K}_3\text{Fe}(\text{CN})_6$ proportionally to the amount of $\text{K}_4\text{Fe}(\text{CN})_6$ and KOH present; the Cu anode requires an alkaline solution. The efficiency of the anode is lowered by deposition of crystals.

(b) Oxidation with a Hg cathode without a diaphragm is not economical. With a diaphragm nearly 100% current efficiency is attained with a c.d. of 0.004–0.005 amp. per sq. cm. The material of the anode does not influence current efficiency. With a Hg cathode and a Ni anode the solution at the anode should be kept alkaline; if the solution is kept neutral, Pt must be substituted for Ni. The final concn. of $\text{K}_3\text{Fe}(\text{CN})_6$ is increased by saturation of the anode solution outside the anodic space.

CHEMICAL ABSTRACTS.

Lead accumulator. I. Changes of resistance at the plates during use. E. DENINA and A. FRATES (Energia Elett., 1931, 8, 8 pp.; Chem. Zentr., 1932, i, 559).—The changes support the theory of double sulphatisation. A. A. ELDRIDGE.

Electrodeposition of ternary alloys of copper, cadmium, and zinc from cyanide baths. R. C. ERNST and C. A. MANN.—See B., 1932, 430.

Electrolytic production of heavy metals from fused electrolytes. III. F. SAUERWALD.—See B., 1932, 430.

[Electrolytic] sodium amalgam formation from sodium chloride solutions. K. S. TESH and H. E. WOODWARD.—See B., 1932, 430.

Action of some organic substances in the electrolytic deposition of zinc. L. CAMBI and G.

DEVOTO (Atti R. Accad. Lincei, 1932, [vi], 15, 27–29).—Addition of pyridine bases to solutions of ZnSO_4 increases the current efficiency for Zn deposition and decreases the deposition potential. Piperidine and analogous bases have no effect. Solutions of NiSO_4 behave similarly in presence of pyridine.

O. J. WALKER.

Deposition of brass from thiocyanate solutions. N. THON and J. PINILLA.—See B., 1932, 387.

Hydrogen peroxide and the Kolbe reaction. S. GLASSSTONE and A. HICKLING (Nature, 1932, 129, 616).—Electrolytic oxidation reactions indicate that H_2O_2 plays an important rôle in certain anodic processes (cf. this vol., 348). L. S. THEOBALD.

Anode phenomena in the electrolysis of potassium acetate. III. Formation of methane. S. N. SHUKLA and O. J. WALKER (Trans. Faraday Soc., 1932, 28, 457–462; cf. A., 1931, 193, 1371).—Electrolysis of KOAc in MeOH , EtOH , and AcOH with low c. d. at a smooth Pt electrode affords results similar to those obtained with aq. KOAc (*loc. cit.*). With aq. KOAc and a Au anode, no hydrocarbons were produced with c. d. between 0.7 and 700 milliamp. per sq. cm., but with Ir and graphite anodes the composition of the evolved gas is similar to that obtained with Pt; the variation of $[\text{AcOH}]$ causes comparatively small changes in the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio.

J. G. A. GRIFFITHS.

Formation of acetylene from methane by the condensed spark at low pressure. R. MONTAGNE (Compt. rend., 1932, 194, 1490–1492; cf. A., 1925, ii, 1194; 1927, 322).—Applying the method previously described to CH_4 at 1–11 mm., the main reaction (to the extent of about 75%) is $2\text{CH}_4=\text{C}_2\text{H}_2+3\text{H}_2$, complicated by subsequent decomp. and condensation of C_2H_2 . The energetic yield is about 15%. The reaction is accelerated and yield, both chemical and energetic, improved by increasing the capacity of the condenser. At the temp. of liquid air up to 10% CH_4 is transformed into saturated or ethylenic hydrocarbons, and the energetic yield is diminished.

C. A. SILBERRAD.

Electric discharges in liquids. I. Arc discharge in water. H. D. CARTER and A. N. CAMPBELL (Trans. Faraday Soc., 1932, 28, 479–496).—The CO_2 , CO , H_2 , saturated hydrocarbons, and O_2 obtained from a specially-designed low-voltage C arc in H_2O were determined. The 1–5% of O_2 is attributed to electrolysis and not to the arcing. The origin of the non-combustible gaseous residue (N_2) was investigated. In addition to particles of C, a solid product similar to "graphitic acid" and a sparingly sol. acid of high m. p. were obtained. With metallic electrodes, hydroxidic substances were produced. The yield of gaseous products increases with rise of temp. of the H_2O , but is independent of pressures as high as 205 lb. per sq. in. The apparent temp. of the C arc, determined by means of an optical pyrometer, is raised from 1300 – 2700° in H_2O at room temp. to 2500 – 3600° with the H_2O at 100° . The mechanism of the process is discussed. In addition to thermal dissociation of H_2O , electrical dissociation of H_2O vapour into H and OH ions is suggested and the form-

ation of solid products is attributed to the reactions of the latter with the electrodes. J. G. A. GRIFFITHS.

Characteristics of polar and non-polar chemical reactions. W. A. WATERS (Proc. Univ. Durham Phil. Soc., 1932, 8, 459—467).—Reactions are classified as non-polar (concerned only with electrically neutral radicals or mols.) and polar (involving the separation of oppositely charged ions). Photochemical activation may be concerned with the former. C. W. GIBBY.

Gaseous photodecomposition of chlorine dioxide. J. W. T. SPINKS (J. Amer. Chem. Soc., 1932, 54, 1689—1690).—The decomp. seems to be a chain reaction. There is an initial decrease in pressure, apparently due to the formation of Cl_2O_6 and its deposition on the walls. The subsequent increase in pressure is probably due to the sensitised decomp. of Cl_2O_6 by Cl atoms. The final rise in pressure closely resembles that observed with a $\text{Cl}_2\text{-O}_3$ mixture. C. J. WEST (c).

Photodecomposition of chlorine dioxide solutions. E. J. BOWEN and W. M. CHEUNG (J.C.S., 1932, 1200—1207).—The main products of the photochemical decomp. of aq. ClO_2 are HClO_3 and HCl in equimol. proportions. The quantum efficiency rises from 0.2 at 4360 Å. to 1.0 at 3000 Å. In CCl_4 solution the limiting quantum efficiency is about 2. The mechanism of reaction is discussed and the results are explained by making use of the observation that gaseous ClO_2 exhibits the phenomenon of predissociation at 3753 Å. E. S. HEDGES.

Hydrazine formation in the synthesis and decomposition of ammonia. I. Synthesis of hydrazine and ammonia by cathode rays. G. R. GEDYE and T. E. ALLIBONE. II. Photochemical decomposition of ammonia. III. Synthesis of hydrazine at catalytic surfaces. G. R. GEDYE and E. K. RIDEAL (J.C.S., 1932, 1158—1160, 1160—1169, 1169—1172).—I. Small yields of NH_3 and N_2H_4 have been obtained by the action of high-velocity electrons on mixtures of N_2 and H_2 . The long range of the electrons renders the method not very suitable for quant. investigation.

II. Investigation of the photochemical decomp. of NH_3 by the total radiation from a quartz-Hg arc by means of a flow method has proved the formation of N_2H_4 . The yield is increased by low temp. of the reaction vessel, a high rate of flow and rapid cooling of the gases leaving the reaction vessel. The yield of N_2H_4 may represent as much as 50% of the decomposed NH_3 . Very little N_2H_4 is obtained in the Hg-sensitised reaction. The decomp. of NH_3 by light is compared with that by ionising radiations.

III. In addition to NH_3 , traces of N_2H_4 are formed when mixtures of H_2 and N_2 are passed over a catalyst of Fe promoted by Al_2O_3 and K_2O . The relative yield of N_2H_4 is greater at lower temp. At 437°, with a very high rate of flow, the yield of N_2H_4 was approx. 4% by wt. of the NH_3 formed. E. S. HEDGES.

Becquerel effect with zinc oxide. E. BÜRGIN (Z. wiss. Phot., 1932, 30, 334—358).—Results are detailed of the nature, permanence, and magnitude of the Becquerel effect with ZnO suspensions in H_2O ,

with and without the addition of cathodic depolarisers (dyes or metallic salts) or anodic depolarisers (glucose, glycerol, benzidine, or NHPH-NH_2), and with and without both. Experiments were made with and without access to air. The electrodes must be shielded from the light to prevent the small effect found to occur on exposure. The formation of ZnO_2 is postulated to account for alternation of the sign of the effect on alternation of exposure to light and dark, the potential rising in the dark, and the ZnO_2 being removed by cathodic depolarisation in the light. Experiments with gas electrodes are described. Baur's theory of sensitised photolysis is supported. J. LEWKOWITSCH.

Theory of the Becquerel effect. E. BAUR (Z. wiss. Phot., 1932, 30, 359—363).—The Becquerel effect is the symptom of a hidden photochemical change in a material system. The application of Baur's theory of sensitised photolysis to explain the effect is upheld. J. LEWKOWITSCH.

Hypersensitisation. I. Influence of silver ions on sensitivity of panchromatic plates. J. I. BOKINIK [with (FRL.) Z. ILJINA]. II. Action of hydrogen peroxide on sensitivity of panchromatic plates. J. I. BOKINIK (Z. wiss. Phot., 1932, 30, 322—329, 330—333).—I. Hypersensitisation by treatment of plates with AgNO_3 before exposure is due to (a) photochemical decomp. of the adsorption complex of AgNO_3 and the sensitising dye, and (b) a very slight effect caused by the strengthening of development by adsorbed Ag ions. TiNO_3 produces only effect (b).

II. H_2O_2 has a desensitising action which is greater in acid than in alkaline solution. Desensitisation of ordinary plates, and hypersensitisation of panchromatic plates, by a solution of AgNO_3 and H_2O_2 (Schmieschek, B., 1930, 793) is due to the action of H_2O_2 and AgNO_3 alone, respectively. N_2H_4 has a strong sensitising action. J. LEWKOWITSCH.

"Antagonism" of radiations in their effects on the photographic plate. E. MÜHLESTEIN (Ann. Guébbard-Séverine, 1930, 6, 123—140).—A summary of the theories of this subject with particular reference to the reversal of image observed in the action of rays from Ra-Em on photographic plates. J. W. SMITH.

Photographic effect of pressure. N. T. ZÉ and C. L. CHAO (Compt. rend., 1932, 194, 1644—1646; cf. A., 1931, 319).—With const. pressure the reduction in density of a photographic plate ($d-d'$) increases as time of exposure increases from that of under- to that of correct exposure, and then decreases for over-exposure. It is also greater for light of shorter wavelength. The relative reduction, $(d-d')/d$, decreases logarithmically as time of exposure increases. C. A. SILBERRAD.

Photographic emulsion: silver-ion and hydrogen-ion concentrations and sensitivity. B. H. CARROLL and D. HUBBARD (Bur. Stand. J. Res., 1932, 8, 481—505).—The rate of after-ripening increases with increasing $[\text{Ag}']$ and increasing p_{H} ; the corresponding effects on sensitivity are much larger than those produced by the direct effect of environment (after digestion). The effect of excess of Ag' is

reduced by combination of Ag^+ with gelatin. The distribution of excess of Br^- or Ag^+ in the emulsion with changing p_{H} has been studied. The desensitising action of Br^- (after digestion) increases with increasing acidity and the effect of p_{H} changes depends on the $[\text{Ag}^+]$. The spectral sensitivity of the emulsions is independent of $[\text{H}^+]$ or $[\text{Ag}^+]$; their influence on sensitivity appears to be through secondary reactions in latent image formation, and of these the elimination of Br^- is better explained by reaction with Ag_2S than with gelatin. The results are explained on the assumption that gelatin is adsorbed by Ag halides in preference to all other materials present. The nature of the adsorption is discussed in the light of the "Zwitterion" theory.

E. S. HEDGES.

Photosynthesis *in vitro*. G. MACKINNEY (J. Amer. Chem. Soc., 1932, 54, 1688—1689).—No procedure yet published enables conditions for obtaining CH_2O and carbohydrates *in vitro* to be reproduced.

C. J. WEST (c).

Progress in the theory of chemical reactions. M. POLANYI (Naturwiss., 1932, 20, 289—296).—A résumé.

W. R. ANGUS.

Alkali fluoborates, alkali fluorosulphonate, and potassium perrhenate. D. VORLÄNDER, J. HOLLATZ, and J. FISCHER (Ber., 1932, 65, [B], 535—538).—The following transition temp. are recorded for the conversion of the feebly doubly-refractive β -forms into the isotropic α -varieties of fluoborates: Na , 239—242°; K , 271—280°; Tl , 203—206°; NH_4 , about 236°. $\text{Ag}(\text{H}_2\text{O})\text{BF}_4$ and LiBF_4 are described. NH_4 , K , and Rb fluorosulphonates are strongly doubly refractive and retain this property until melted or decomposed; they differ crystallographically from perchlorates and fluoborates. KReO_4 does not exhibit dimorphism.

H. WREN.

Alkali phosphates. I. Sodium pyrophosphate and the reaction pyrophosphate \rightleftharpoons orthophosphate. H. MENZEL and L. SIEG [with F. EBERT] (Z. Elektrochem., 1932, 38, 283—299).—The literature relating to analysis of ortho- and pyro-phosphates is critically reviewed, and the Debye-Scherrer diagrams of the Na salts and their various hydrates are described. The solubility curve (0—96°) of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ shows that transition to the anhyd. salt occurs at 79.5°; no other hydrate appears to exist. V.-p. measurements in the system $\text{Na}_4\text{P}_2\text{O}_7$ — $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ between 20° and 80° yield for the heat of hydration 124.5 kg.-cal. The action of dry gaseous or liquid NH_3 on $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ yields the anhyd. salt, but no ammoniate is produced at temp. down to -78.5°. $\text{Na}_4\text{P}_2\text{O}_7$ has m. p. $980^\circ \pm 2^\circ$; only one cryst. form exists between room temp. and the m. p. The isothermal decomp. of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ at 20°, and the v. p. of saturated solutions of this salt and of both the lower hydrates (7 and $2\text{H}_2\text{O}$) have been studied; the conditions necessary for the prep. of each hydrate are described. Thermal analysis does not serve to elucidate fully the reaction $2\text{Na}_2\text{HPO}_4 \rightarrow \text{Na}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$. Measurement of the decomp. pressure of Na_2HPO_4 between 130° and 208° is difficult, and the p - T curve obtained may represent either a univariant equilibrium between one vapour and two

solid phases, or a more complex process. Isothermal dehydration of Na_2HPO_4 at 211° yields cryst. $\text{Na}_4\text{P}_2\text{O}_7$; at 131° an amorphous form is produced, and this at a suitable H_2O v. p. may be reconverted into Na_2HPO_4 . The cryst. form of $\text{Na}_4\text{P}_2\text{O}_7$ combines very slowly with H_2O at 131°, and the equilibrium pressure is markedly higher than in the case of the amorphous salt.

H. F. GILLBE.

Formation of cupric sulphide, selenide, and telluride. H. PÉLABON (Bull. Soc. chim., 1932, [iv], 51, 377—380).—When Cu and S (Se or Te) are placed in contact in a solution of CuSO_4 , $\text{Cu}(\text{NO}_3)_2$, or $\text{Cu}(\text{OAc})_2$, CuS is formed with a velocity depending on the concn. of the Cu^{++} solution. The same effect is obtained if the Cu and S are joined by an electrical conductor such as Pt wire and also when solid S is replaced by a solution in CS_2 . The action is due to the formation of an electrolytic cell and a p. d. of about 0.2 volt has been observed. Thomson's formula is applicable.

E. S. HEDGES.

Conditions of reduction of Fehling's solution. A. HEIDUSCHKA and W. BIETHAN (J. pr. Chem., 1932, [ii], 133, 273—283).—The amount of auto-reduction of Fehling's solution increases as the following factors increase: time of heating, time of exposure to O_2 , concn. of the solution, and concn. of CuSO_4 , alkali, or NaK tartrate. A method, involving addition of $\text{K}_4\text{Fe}(\text{CN})_6$ to Fehling's solution, is described for determining glucose in 0.1—0.5% solution. By the modified process the amount of CuO reduced is exactly proportional to the amount of glucose oxidised; the results are independent of the time of heating and concn. of CuSO_4 , $\text{K}_4\text{Fe}(\text{CN})_6$, or alkali, but air must be excluded. Auto-reduction is influenced by the same factors as in the absence of this salt and is also increased by addition of glycerol and NaOH . By the modified process 1 mol. of glucose absorbs 4 atoms of O_2 , contrasted with 2—2.25 atoms by the usual method. Schaer's interpretation (Chem.-Ztg., 1904, 27, 912) of the auto-reduction is considered to be supported by the above results.

R. S. CAHN.

Berthollet's silver fulminate. P. C. VAN DER WILLIGEN (Chem. Weekblad, 1932, 29, 232).—An account of an explosion during the prep. of a small quantity of ammoniacal Ag solution.

S. I. LEVY.

Beryllium. H. BORCHERS (Metall-Wirt., 1931, 10, 863—866; Chem. Zentr., 1932, i, 510).—Experiments in H_2 from low to atm. pressure gave no indication of compound formation; no change takes place in moist air, H_2O , or H_2O vapour. Finely powdered Be burns brightly in air; when heated in air it forms a white surface layer 200—300° below the f. p., and with rising temp. the metal is completely converted into this substance, a mixture of nitride and oxide. At higher temp. Be is very sensitive towards small quantities of O_2 . Above 1400° Be attacks SiO_2 , presumably forming BeO and Si . Al_2O_3 is analogously reduced by Be . The m. p., which depends on the purity, is 1285°, and the calc. heat of fusion is 345.5 g.-cal. The purity and electrolytic purification of Be are discussed.

A. A. ELDRIDGE.

Fluoberyllates and their analogy with sulphates. II. Fluoberyllates of bivalent metals.

N. N. RAY (Z. anorg. Chem., 1932, 205, 257—267; cf. this vol., 131).—The following salts have been prepared: CaBeF_4 , d_4^{30} 2.959; SrBeF_4 , d_4^{30} 3.736; $\text{NiBeF}_4 \cdot 7\text{H}_2\text{O}$; $\text{NiBeF}_4 \cdot 6\text{H}_2\text{O}$, d_4^{30} 1.941; $\text{NiBeF}_4 \cdot 3\text{H}_2\text{O}$; $\text{CoBeF}_4 \cdot 7\text{H}_2\text{O}$, d_4^{30} 1.867; $\text{CoBeF}_4 \cdot 6\text{H}_2\text{O}$, d_4^{30} 1.891; $\text{CoBeF}_4 \cdot 3\text{H}_2\text{O}$; $\text{CoBeF}_4 \cdot 2\text{H}_2\text{O}$; $\text{ZnBeF}_4 \cdot 7\text{H}_2\text{O}$; $\text{CdBeF}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$; $\text{FeBeO}_4 \cdot 7\text{H}_2\text{O}$, d_4^{30} 1.894; $\text{CuBeF}_4 \cdot 5\text{H}_2\text{O}$. The Ni, Co, Zn, Fe^{II} , Cd, and Cu salts are isomorphous with the corresponding sulphates. F. L. USHER.

Trimagnesium phosphate. C. ZINZADZÉ (Compt. rend., 1932, 194, 1498—1500).—To obtain $\text{Mg}_3(\text{PO}_4)_2$ the p_{H} of the solution must be < 13 ; with greater acidity increasing quantities of MgHPO_4 result, and this alone with $p_{\text{H}} > 8$. To prepare $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$, 2 parts of 20% aq. MgSO_4 (d^{15} 1.222) and 1 of 9% aq. Na_3PO_4 (d^{15} 1.1) are agitated together, and the ppt. is washed by decantation with less H_2O than was present at the first mixing. Drying must be effected below 30° (cf. A., 1924, ii, 676; B., 1926, 841; 1927, 55). C. A. SILBERRAD.

Perovskite (CaO, TiO_2) and titanite ($\text{CaO}, \text{TiO}_2, \text{SiO}_2$). K. IWASÉ and M. FUKUSIMA (Bull. Chem. Soc. Japan, 1932, 7, 91—102).—Perovskite and titanite were prepared by fusing together their constituents, using CaCO_3 instead of CaO . In the prep. of titanite, if the melt was allowed to supercool below about 1280° , perovskite and SiO_2 separated together with the titanite. Above this temp. only titanite separated, this compound being more stable than the mixture $\text{CaO}, \text{TiO}_2 + \text{SiO}_2$. This mixture melts at about 1390° , titanite at 1383° , Na_2SiO_3 at 1088° , Li_2SiO_3 at 1202° . D. R. DUNCAN.

Calcium aluminates. II. Crystallisation of calcium aluminate solutions at 40° . G. ASSARSON (Z. anorg. Chem., 1932, 205, 335—360).—The compounds crystallising from a mixture of freshly-prepared solutions of Ca aluminate and $\text{Ca}(\text{OH})_2$ at 40° have been investigated optically and analytically and the results recorded in a triangular diagram. The same aluminates have been identified as were previously obtained at 20° (A., 1931, 1370). Al hydroxide forms as a gel and also as a crypto- and micro-cryst. aggregate. The form first obtained has the composition $\text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, but the one obtained later is probably hydrargillite or bayerite. Pure aluminates separate from those solutions in which the mol. proportions $\text{CaO} : \text{Al}_2\text{O}_3 > 2$, the tetra-aluminate being always the first formed and other compounds following when the crystallisation of this is complete. Al hydroxide separates if the proportion lies between 1 and 2. Within a certain dilution range these solutions are metastable and deposit no Al hydroxide, although they cannot be unsaturated.

M. S. BURR.

Hydrothermal synthesis of calcium silicates under ordinary pressure. III. S. NAGAI (J. Soc. Chem. Ind. Japan, 1932, 35, 153—156B; cf. A., 1931, 1020, 1380).—A 1:1 $\text{CaO}-\text{SiO}_2$ mixture heated at $800-900^\circ$ first yields $3\text{CaO}, 2\text{SiO}_2$ but on further heating gives CaO, SiO_2 . A 3:2 $\text{CaO}-\text{SiO}_2$ mixture treated similarly yields at first $3\text{CaO}, 2\text{SiO}_2$, then $2\text{CaO}, \text{SiO}_2$. If CaO is replaced by CaCO_3 in

these and previous experiments results are not affected except by the time required to decompose the CaCO_3 .

C. IRWIN.

Action of thiocyanates on mercurous salts. J. FIALKOV (Z. anorg. Chem., 1932, 205, 235—240).—The transformation of Hg_2^{++} into $\text{Hg} + \text{Hg}^{++}$ is practically complete in presence of excess of KCN , owing to the removal of Hg^{++} as a complex anion. The reaction has been used for the determination of Hg^{I} .

F. L. USHER.

Inhomogeneity of highly active salt of radium barium chloride. F. BÉHOUNEK and O. KOBLEC (Physikal. Z., 1932, 33, 376—378).—The inhomogeneity is a primary property and arises from the concn. of RaCl_2 .

A. J. MEE.

Reactions of boron fluoride with alcohols and glycols. T. H. VAUGHN, H. BOWLUS, and J. A. NIEUWLAND (Proc. Indiana Acad. Sci., 1931, 40, 203—206).—The acidic substance formed when BF_3 is passed into MeOH is a co-ordination compound. When C_2H_2 is passed into MeOH containing BF_3 , MeOH , acetal is formed. Et_2O inhibits the reaction owing to preferential formation of a non-ionised compound with BF_3 .

CHEMICAL ABSTRACTS.

Valency relations of halides of periodic groups III, IV, and V. W. M. FISCHER and A. TAURINSCH (Z. anorg. Chem., 1932, 205, 309—320; cf. A., 1931, 613).—The following compounds with $\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ (1:4) are described (figures denote temp. of decomp.; $\text{M}=\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$): $2\text{M}, \text{BCl}_3$ 166°; $3\text{M}, \text{BCl}_3$ 158°; $3\text{M}, \text{AlBr}_3$ 155°; $3\text{M}, 2\text{AlBr}_3$ 184—190°; $2\text{M}, \text{AlBr}_3$ 160—175°; $3\text{M}, \text{AlCl}_3$ 170°; $3\text{M}, 2\text{AlCl}_3$ 182—184°; $4\text{M}, \text{SiCl}_4$ 163°; $8\text{M}, \text{SiCl}_4$ 200°; M, SiHCl_3 166°; $2\text{M}, \text{TiCl}_4$ 215°; M, TiCl_4 230°; $\text{M}, 2\text{SnCl}_2$ 110—112°; M, SnCl_4 50—55°; $2\text{M}, \text{SnCl}_4$; $2\text{M}, \text{SnBr}_4$ 65°; $2\text{M}, \text{ThCl}_4$ 210°; $3\text{M}, \text{PBr}_3$ 163—164°; $5\text{M}, \text{PCl}_5$ 172°; $5\text{M}, \text{PBr}_5$ 172°, 194°; $2\text{M}, \text{PhOPCl}_2$ 171°; $4\text{M}, \text{PhOPCl}_4$ 170—173°; $3\text{M}, (\text{PhO})_2\text{PCl}_3$ 170—174°; $2\text{M}, \text{PI}_3$ 96°; $3\text{M}, \text{AsCl}_3$ 175—176°; M, SbCl_5 151°; $2\text{M}, 3\text{SbCl}_5$ 124°. The formation of the compounds is discussed with reference to the equivalence or otherwise of the halogen atoms.

F. L. USHER.

Action of anhydrous aluminium chloride (bromide) on some aliphatic alcohols and acetone. H. FUNK, J. SCHORMÜLLER, and W. HENSINGER (Z. anorg. Chem., 1931, 205, 361—368; cf. A., 1931, 1020).—The following compounds have been prepared by the action of AlCl_3 or AlBr_3 on some alcohols and COMe_2 : $\text{AlCl}_2(\text{OMe}), 2\text{AlCl}_3, 16\text{MeOH}$; $\text{Al}_3\text{Cl}_2\text{O}_2(\text{OMe})_3$ which may have either of the structural formulæ $2\text{AlOCl}, \text{Al}(\text{OMe})_3$ or $2\text{AlO}(\text{OMe}), \text{AlCl}_2(\text{OMe})$;

$\text{AlCl}_2(\text{OEt}), 2\text{AlCl}_3, 10\text{EtOH}$;

$\text{AlBr}_2(\text{OMe}), 2\text{AlBr}_3, 16\text{MeOH}$;

$\text{AlBr}_2(\text{OEt}), 2\text{AlBr}_3, 15\text{EtOH}$;

$\text{AlCl}_2(\text{OPr}), 2\text{AlCl}_3, 5\text{PrOH}$;

$\text{AlCl}_2(\text{OMe}), \text{AlCl}_3, 8\text{MeOH}$; $\text{Al}_5\text{Cl}_9\text{O}(\text{OMe})_4$;

$\text{AlCl}_2(\text{CH}_2\cdot\text{COMe}), \text{AlCl}_3, 2\text{COMe}_2$.

M. S. BURR.

Hydrothermal synthesis of muscovite. W. NOLL (Naturwiss., 1932, 20, 283).—Muscovite ($\text{K}_2\text{O}, 3\text{Al}_2\text{O}_3, 6\text{SiO}_2$) was prepared by heating an aq. solution of the corresponding colloid adsorption compound in a pressure bomb for 5 days at 300° .

The prep. thus obtained was identified as muscovite by its *X*-ray interference pattern. W. R. ANGUS.

Zeolites and salts slightly soluble in water. G. AUSTERWEIL (Compt. rend., 1932, 194, 1581—1583; cf. this vol., 30).—The whole salt, both cation and anion, can be removed from a solution by a zeolite saturated with a mobile cation that forms an insol. compound with the anion in solution, provided that this is more sol. than the resultant zeolite. Thus a zeolite saturated with a Pb salt will entirely remove Na_2CrO_4 or K_2CO_3 from aq. solution, PbCrO_4 or PbCO_3 being pptd. in the interstices of the zeolite. Conversely a Na zeolite, mixed with the correct amount of powdered $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, on lixiviation with H_2O yields an almost theoretical amount of Na_2SO_4 . It is impossible to extract Na_2CO_3 by lixiviating with H_2O a mixture of a Na zeolite and CaCO_3 , as CaCO_3 is less sol. than the resultant Ca zeolite.

C. A. SILBERRAD.

Compounds of higher valency in the rare earths. I. Lanthanum oxide. G. JANTSCH and E. WIESENBERGER (Monatsh., 1932, 60, 1—7).—Contrary to Kolthoff and Elmquist (A., 1931, 702) no appreciable increase in wt. is observed when La_2O_3 is heated at 1000—1300° in dry O_2 or air or in moist air. When a Pt boat is used slight adsorption of Pt by the oxide occurs.

H. A. PIGGOTT.

Anhydrous chlorides of the cerium group metals. P. BRAUMAN and S. TAKVORIAN (Compt. rend., 1932, 194, 1579—1580).—Excess of aq. NaOBz ppts. a neutral or slightly acid solution of a salt of La, Nd, Sm, etc. completely as $\text{M}(\text{OBz})_3 \cdot 3\text{H}_2\text{O}$, which is completely dehydrated at 110°. The anhyd. benzoate is treated with dry Et_2O saturated with HCl, the product washed with Et_2O , and treated with HCl at 60° and finally with dry air. The pure anhyd. chloride MCl_3 results.

C. A. SILBERRAD.

Germanium. IX. Germanates of alkali and alkaline-earth metals. R. SCHWARZ and F. HEINRICH (Z. anorg. Chem., 1932, 205, 43—48; cf. this vol., 117).—*M*-*p*. curves of the systems $\text{Na}_2\text{O}-\text{GeO}_2$ and $\text{K}_2\text{O}-\text{GeO}_2$ indicate the existence of the following compounds (m. p. in parentheses): Na_2GeO_3 (1083°), $\text{Na}_2\text{Ge}_2\text{O}_5$ (799°), *Na tetragermanate* $\text{Na}_2\text{Ge}_4\text{O}_9$ (1052°); K_2GeO_3 (842°), $\text{K}_2\text{Ge}_2\text{O}_5$ (797°), $\text{K}_2\text{Ge}_4\text{O}_9$ (1038°). Each pair of salts forms a eutectic. Li_2GeO_3 forms no hydrate, Na_2GeO_3 a hexa- and hepta-hydrate. SrGeO_3 (anhyd.) and BaGeO_3 ($4\text{H}_2\text{O}$ and $5\text{H}_2\text{O}$) can be obtained cryst. from aq. solution, but not metagermanates of K, Mg, and Ca. F. L. USHER.

Influence of fusible reaction products or of preformed eutectics on the extent of interaction in mixed powders. J. A. HEDVALL and I. BERGSTRAND (Z. anorg. Chem., 1932, 205, 251—256; cf. A., 1931, 803).—The reaction between solid PbCl_2 and CaO is not appreciably influenced by small quantities of the fused reaction products or of an added fusible substance, but is considerably increased by quantities of the order of 40%. If the eutectic in question (*e.g.*, $\text{PbCl}_2-\text{AgCl}$) is previously formed the effect is much more pronounced. F. L. USHER.

Mechanism of precipitation processes. IX. Reaction between lead bromide and sulphide

ions. Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anorg. Chem., 1932, 205, 268—272; cf. A., 1931, 323).—The reaction $2\text{PbBr}^+ + \text{S}'' = \text{Pb}_2\text{Br}_2\text{S}$ occurs to a considerable extent when solutions of PbBr_2 and Na_2S are mixed. The amount of $\text{Pb}_2\text{Br}_2\text{S}$ in the ppt. decreases with time, and its formation is repressed by dilution, by increasing $[\text{H}^+]$ (except with HBr), by increasing the ratio $\text{Na}_2\text{S} : \text{PbBr}_2$, or by carrying out the pptn. more slowly. $\text{Pb}_2\text{Br}_2\text{S}$ is a red cryst. substance, stable at 70—80°, and is sol. in H_2O at 20° to the extent of 3.5×10^{-5} mol. per litre.

F. L. USHER.

Thorium nitride. Determination of nitrogen in incombustible inorganic substances. W. DÜSING and M. HÜNIGER (Tech. wiss. Abh. Osram-Konz., 1931, 2, 357—365; Chem. Zentr., 1932, i, 203—204).—By decomp. of Th halide at a glowing W wire in N_2 small quantities of a nitride having low electrical conductivity are formed. Compressed ThO_2 , graphite, and W are electrically heated at 2220—2600° in a non-oxidising atm. containing N_2 ; black crystals of Th_3N_4 are formed. In presence of traces of O_2 the crystals are coloured yellow or red owing to the presence of ThO_2 . For analysis the substance is melted in a Pt boat with $\text{Na}_2\text{S}_2\text{O}_7$ and the N_2 collected over alkaline pyrogallol solution.

A. A. ELDRIDGE.

Mechanism of the reaction between persulphate and iodide ions. A. VON KISS and I. BOSÁNYI (Rec. trav. chim., 1932, 51, 434—444; cf. A., 1929, 772).—A reply to criticisms by King and Jette and by Oostveen (A., 1929, 771, 1016). Earlier work has been repeated and its accuracy is confirmed.

F. L. USHER.

Selenites of sodium and potassium. J. JANITZKI (Z. anorg. Chem., 1932, 205, 49—76).—Solubilities of normal and acid selenites of Na and K have been determined, and the composition of the salts and their hydrates has been established by analysis. The hydrates $\text{Na}_2\text{SeO}_3 \cdot 8\text{H}_2\text{O}$, $\text{NaHSeO}_3 \cdot 3\text{H}_2\text{O}$, and $\text{K}_2\text{SeO}_3 \cdot 4\text{H}_2\text{O}$ have been prepared. MHSeO_3 and $\text{M}_2\text{Se}_2\text{O}_5$ are interconvertible in aq. solutions containing $\text{M}_2\text{O} + 2\text{SeO}_2$, whereas those containing $\text{M}_2\text{O} + 4\text{SeO}_2$ yield $\text{MH}_2(\text{SO}_3)_2$ only. The p_{H} of 0.05 or 0.1*N* solutions of all the salts has been determined. Na_2SeO_3 is hydrolysed about 0.1% at 0.1*N* concn.

F. L. USHER.

Oxidation of chromium hydroxide and chromite by atmospheric oxygen in presence of alkali. V. V. IPATIEV, jun., and M. N. PLATONOVA (Ber., 1932, 65, [B], 572—575).—Oxidation of $\text{Cr}(\text{OH})_3$ by air at 300°/100 atm. is quant. after 18 hr. in presence of sufficient KOH to give K_2CrO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$. The change occurs also in presence of K_2CrO_4 solution. Diminution of temp. delays the reaction, which does not occur in absence of O_2 pressure. The rate of reaction decreases rapidly with fall in OH' concn. Finely-divided chromite is oxidised more slowly than $\text{Cr}(\text{OH})_3$. Reaction does not occur in K_2CrO_4 solution. It is hastened by elevated temp. and an excess of alkali. 60% of the available Cr can be oxidised.

H. WREN.

Complex cyanide of tervalent molybdenum. R. C. YOUNG (J. Amer. Chem. Soc., 1932, 54, 1402—

1405).—The interaction of K_3MoCl_6 and KCN at room temp. in an atm. of N_2 gives the black compound $K_4Mo(CN)_7 \cdot 2H_2O$. B. A. SOULE (c).

Oxygen compounds containing fluorine. II. H. SEIFERT (Z. Krist., 1932, 82, 15—30; cf. this vol., 449).—Some more complicated "double salts," e.g., $(NH_4)_2MoOF_5$, $(NH_4)_3MoO_2F_5$, $K_5U_2O_4F_9$, etc., and minerals such as the humite-chondrodite series, are discussed on similar lines. Certain other compounds are shown to be "false," i.e., the F is not directly connected with the central atom, e.g., $R_3HS_2O_7 \cdot F_2 \cdot H_2O$ ($R=K, Rb, Cs$) (cf. A., 1899, ii, 594), which are really only $2RHSO_4 \cdot RF \cdot HF$. C. A. SILBERRAD.

Chlorine hydrate. S. ANWAR-ULLAH (J.C.S., 1932, 1172—1176).—Under different conditions of temp., pressure, and concn. of the constituents, Cl hydrate has the composition $Cl_2 \cdot 6H_2O$. The higher hydrates previously recorded probably indicate incomplete reaction or imperfect drying.

E. S. HEDGES.

Bromine chloride hydrate. S. ANWAR-ULLAH (J.C.S., 1932, 1176—1179).—Cryst. $BrCl \cdot 4H_2O$ is obtained by passing Cl_2 into Br under a layer of H_2O at temp. below 18° . It is more stable than the hydrates of Cl_2 or Br. The solubility of Br in H_2O is considerably enhanced by the presence of Cl_2 .

E. S. HEDGES.

[Reactions of iodine.] E. ABEL (Z. physikal. Chem., 1932, 159, 414).—Polemical against Angelescu and Popescu (A., 1931, 1369, 1372). R. CUTHILL.

Dehydration of salts with organic liquids. J. G. F. DRUCE (Chem. News, 1932, 144, 199—200).—By distilling PhMe over $MnSO_4 \cdot 4H_2O$ the salt was converted into the monohydrate. With $PhNO_2$ or a saturated hydrocarbon oil of b. p. $190-195^\circ$ dehydration was carried a stage further and the anhyd. salt was formed. Both $MnSO_4 \cdot 4H_2O$ and $CuSO_4 \cdot 5H_2O$ could be completely dehydrated by warming with Ac_2O without having recourse to distillation (cf. Stephen, A., 1931, 182).

A. B. MANNING.

Highest oxide of rhenium. H. V. A. BRISCOE, P. L. ROBINSON, and A. J. RUDGE (Nature, 1932, 129, 618).—Evidence that Re_2O_7 is the highest oxide of Re stable under ordinary conditions is advanced. The m. p. of Re_2O_7 is lowered by traces of H_2O and a specimen of m. p. approx. 150° gave a white sublimate without an increase in wt. $KMnO_4$ was not decolorised by any sublimates from Re_2O_7 (cf. A., 1929, 411).

L. S. THEOBALD.

Rhenium oxychloride. H. V. A. BRISCOE, P. L. ROBINSON, and A. J. RUDGE (J.C.S., 1932, 1104—1107).— ReO_2Cl_3 is prepared by heating (a) Re in dry mixtures of air and Cl_2 , (b) $ReCl_4$ in dry O_2 , (c) Re_2O_5 in dry Cl_2 . Method (a) is the most convenient. ReO_2Cl_3 has m. p. $23.9 \pm 0.2^\circ$; the liquid has d_{25}^{35} 3.359 and vaporises in vac. below 300° . It is decomposed by H_2O .

E. S. HEDGES.

Thermite reaction with rhenium dioxide. J. G. F. DRUCE (Chem. News, 1932, 144, 247).—A mixture of ReO_2 and Al, ignited by means of a Mg fuse, yields Al_2O_3 and amorphous Re, which may be separated by treatment with HCl; fused Re could not

be obtained by this method. The product closely resembles that formed by reduction of ReS_2 by H_2 .

H. F. GILLBE.

Hydroxides and carbonates of metals. I. Ferric hydroxide. A. V. RAKOVSKI. II. Chromic hydroxide. A. V. RAKOVSKI and T. POLJANSKI (Trans. Inst. Pure Chem. Reag. U.S.S.R., 1931, No. 12, 3—10, 11—16).—I. The compositions of $Fe_2O_3 + H_2O$ gels prepared and dried under different conditions are given. Gels obtained by pptg. Fe^{+++} salts with alkali hydroxide or carbonate always contain CO_2 (up to 3%), which varies in amount with the H_2O present. Admixed SO_4^{--} , Cl^- , etc. cannot be washed out of the gels but may be displaced by CO_3^{--} .

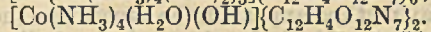
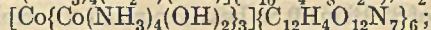
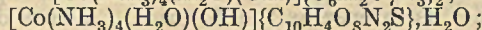
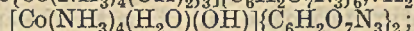
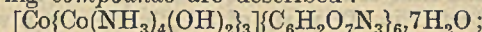
II. Cr hydroxide free from Cl^- may be obtained by reducing $Na_2Cr_2O_7$ with CH_2O in presence of HCl, pptg. with NH_3 , and washing with dil. NH_3 and then with H_2O . Preps. made from the sulphate cannot be freed completely from SO_4^{--} . CO_2 is present in all the hydroxides obtained, which may be regarded as Cr carbonates in a dissociated state. Isotherms showing the relation of $(CO_2 + H_2O)$ in the hydroxides to the v. p. of H_2O in the surrounding air reveal hysteresis, which virtually disappears after repeated hydration and dehydration.

T. H. POPE.

Ammines. V. Dihydroxotetramminocobaltic hydroxide and its derivatives. H. J. S. KING (J.C.S., 1932, 1275—1281).—The chemical reactions of the hydroxide solution obtained when

$[Co(H_2O)_2(NH_3)_4]Cl_3$ is triturated with moist Ag_2O indicate the formula $[Co(NH_3)_4(H_2O)(OH)](OH)_2$ and no solid salts corresponding with a dihydroxotetramminocobaltic series can be isolated, even with acids which usually form very sparingly sol. salts of the type. Electrical conductivity measurements, however, support the formula $[Co(NH_3)_4(OH)_2]OH$. Corresponding salts appear to exist in solution, for concordant vals. for the mobility of $[Co(NH_3)_4(OH)_2]^+$ are obtained in these solutions. The mobilities of

$[Co(NH_3)_4(H_2O)(OH)]^{++}$ and $[Co(NH_3)_4(OH)_2]^+$ at 0° are 60.8 and 23.0 mhos, respectively. The following compounds are described:



E. S. HEDGES.

Mode of formation of the cobaltite modification of Rinman's green. J. A. HEDVALL and T. NILSSON (Z. anorg. Chem., 1932, 205, 425—428).—The reaction by which the cobaltite modification of Rinman's green is formed is in accordance with the equation $ZnO + CoO, Co_2O_3 = ZnO, Co_2O_3 + CoO$ and is not an additive reaction between ZnO and Co_2O_3 . The instability of Co_2O_3 , even in O_2 , when heated below 300° is confirmed. Co_3O_4 is stable in air up to 900° , but above this temp. it is dissociated into CoO and O_2 . CoO is readily oxidised to Co_3O_4 . M. S. BURR.

Higher oxides of group VIII elements. Structure of nickel oxide hydrates. D. K. GORALEVITSCH (J. Gen. Chem. Russ., 1931, 1, 973—990).—The compounds $Ni_2O_3 \cdot 3, 4, 5,$ and $6H_2O$, and $Ni_3O_4 \cdot 2,$

3, 5, and $6\text{H}_2\text{O}$ are formed when Cl_2 or Br is passed through alkaline solutions of $\text{Ni}(\text{OH})_2$. Part of the H_2O of these compounds is constitutional, being eliminable only at temp. $>120^\circ$, whilst the remainder is H_2O of crystallisation. The above compounds are hydrates of the acids $\text{H}_4\text{Ni}_2\text{O}_5$, $\text{H}_4\text{Ni}_3\text{O}_6$, $\text{H}_2\text{Ni}_2\text{O}_4$, and $\text{H}_2\text{Ni}_3\text{O}_5$. The relative proportions of these compounds in the product depend on the relative concn. of $\text{Ni}(\text{OH})_2$ and $\text{Ni}(\text{OH})_3$ at the moment of action of NaOBr or NaOCl . The structural formulæ of the above acids and of certain of their salts are discussed.

R. TRUSZKOWSKI.

Improved method of quantitative spectrographic analysis. C. C. NITCHE and G. W. STANDEN (Ind. Eng. Chem. [Anal.], 1932, 4, 182—185; cf. A., 1929, 412).—The element is determined by measuring the intensity of one of its spectrum lines and comparing with the intensity of another line in the same spectrum due to another constituent known to be present in const. amount in all the samples. A recording microphotometer for measuring the intensities has been constructed. The max. deviation of the analyses from the mean is about 5% in the determination of 0.01% of Mg in an alloy, the chief error being connected with the excitation of the spectra.

E. S. HEDGES.

Molecular spectra and spectroscopic analysis. G. PICCARDI (Atti R. Accad. Lincei, 1931, [vi], 14, 578—582).—The usefulness of band spectra in qual. and quant. spectroscopic analysis is discussed.

O. J. WALKER.

Sensitivity of atomic analysis by X-rays. C. E. EDDY and T. H. LABY (Proc. Roy. Soc., 1932, A, 135, 637—656).—It is confirmed that a sensitivity of 1 or even 0.1 p.p.m. of a metallic element in an alloy can be obtained by at. analysis by X-ray spectroscopy (A., 1929, 867), but the sensitivity is greatly reduced when a poor vac. exists in the X-ray tube and when scattered radiation reaches the photographic plate. The conditions influencing the sensitivity are discussed. Although theoretically the sensitivity for an element of low at. no. alloyed with one of high at. no. should be less than that of the reverse case, 1 part of 29 Cu can be detected in 10^6 parts of 82 Pb. For equiv. conditions of excitation the lines in the K series are approx. 20 times as intense as the L series. L lines due to 0.002% of 83 Bi in 50 Sn have, however, been observed. The X-ray method appears to be superior to the optical and chemical methods for the analysis of alloys.

L. L. BIRCUMSHAW.

Modern micro-chemical methods. K. JOSEPHSON (Svensk Kem. Tidskr., 1932, 44, 98—115).—A review.

Polarographic studies with the dropping mercury cathode. XXV. Increased sensitivity of micro-analytical determinations by compensation of current. D. ILKOVIČ and G. SEMERANO (Coll. Czech. Chem. Comm., 1932, 4, 176—180).—By compensating for the current required for charging the repeatedly renewed surface of the dropping Hg cathode, the sensitivity of polarographic analyses of electro-reducible substances has been increased 10-fold. A suitable circuit is described. In general, 5×10^{-7} g.-equiv. of reducible substance per litre,

i.e., 10^{-9} to 10^{-8} g. in the 0.2 c.c. of solution required, may be detected.

H. F. GILLBE.

Electrometric determination of p_{H} . H. D. VAN OORT (Intern. Sugar J., 1932, 34, 95—98).—Using the automatic H electrode apparatus for recording p_{H} (B., 1932, 431), a lightly platinised electrode was rapidly affected by As_2O_3 , but buffer solutions to which brucine sulphate, indigo-carmin, KCN, KCNS, and Na_2S had been added failed to show any distinct poisoning effect. The nature of the poisoning observed in the case of beet juice was not ascertained.

J. P. OGILVIE.

Hydrogen effect as a source of error in p_{H} measurements. L. WOLF, (FRL.) L. P. USPENSKAJA, and K. ASKITOPOULOS (Naturwiss., 1932, 20, 297).—The H effect depends on the size of the electrode. p_{H} measurements on $M/30$ -phosphate + N -KCl and on $M/120$ - Na_2HPO_4 + N -KCl are given.

W. R. ANGUS.

Electrometric determination of the p_{H} using an antimony electrode. M. CATENACCI (L'Ind. sacc. Ital., 1931, 24, No. 8; Int. Sugar J., 1932, 34, 185).—An Sb electrode consists of a rod of the metal sealed into one end of a piece of glass tubing filled with Hg, and a wire connecting the Hg with the Hg_2Cl_2 cell. It functions at any p_{H} , and is unaffected by the presence of NH_3 , SO_2 , protein, and colloidal substances as found in sugar-factory products. Equilibrium is quickly established, and it gives results sufficiently accurate for technical work.

J. P. OGILVIE.

p_{H} chart. G. H. BELL and A. R. C. PATERSON (Biochem. J., 1932, 26, 454—457).—A chart is constructed to facilitate calculations on the measurement of p_{H} by the H electrode from p_{H} 1.5 to 12.0 at 18 — 25° .

S. S. ZILVA.

Bimetallic electrodes with nichrome in potentiometric acidimetry. A. MAZZUCHELLI (Gazzetta, 1932, 62, 265—270).—Nichrome and Pt in presence of a little H_2O_2 form a satisfactory pair of electrodes for potentiometric acidimetry. The p.d. across the electrodes is measured by means of a triode valve potentiometer.

O. J. WALKER.

Use of metallic electrodes as indicators. S. J. FRENCH and J. M. HAMILTON (Proc. Indiana Acad. Sci., 1931, 40, 171—174).—A review. In the titration of HCl, HNO_3 , and H_2SO_4 the pair Al/Rose-metal gives accurate results.

CHEMICAL ABSTRACTS.

Sinalbin as an indicator. K. HARRISON (Biochem. J., 1932, 26, 88—89).—The glucoside of white mustard seeds (0.5% in 30% EtOH) is a suitable indicator for titration of weak acids and bases. The p_{H} range is 6.2 (colourless)—8.4 (yellow). Salt and protein errors are small.

A. COHEN.

Indicators. I. 2:6-Dinitrophenol. I. V. KULIKOV and S. V. PANOVA. II. Iodoeosin. I. V. KULIKOV and A. G. PUKIREV (Biochem. Z., 1932, 246, 87—96, 97—103).—I.—A method is described for nitration of *o*-nitrophenol in AcOH and H_2SO_4 , the method giving 30—35% of 2:6-dinitrophenol. II.—The I content of iodoeosin is determined by fusion with NaOH + NaNO_3 and the iodate reduced with H_2SO_3 . Iodoeosin from different sources

shows somewhat different degrees of iodination, but this does not affect its use as an indicator.

P. W. CLUTTERBUCK.

Micro-determination of water in coal and other solid materials. F. VETTER.—See B., 1932, 403.

Potentiometric determination of bromine, and octovalent and quadrivalent osmium in hydrobromic acid solutions. II. W. R. CROWELL (J. Amer. Chem. Soc., 1932, 54, 1324—1328; cf. A., 1929, 1029).—By heating Os^{VIII} at 100° in the presence of approx. 8*N*-HBr in a sealed tube, it becomes quadrivalent; an equiv. quantity of Br is liberated, and can be titrated potentiometrically with aq. $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$. Similar treatment in approx. 0.1*N*-HBr causes complete oxidation of Os^{IV} to Os^{VIII} , and the excess of Br after heating measures the Os content. Because of its greater stability, N_2H_4 is better than TiCl_3 for titrating Br solutions.

W. T. HALL (c).

Calcium fluoride method for determination of fluoride, with special reference to analysis of nickel-plating solutions. S. G. CLARKE and W. N. BRADSHAW.—See B., 1932, 382.

Determination of fluorine. P. MOUGNAUD (Compt. rend., 1932, 194, 1507—1509; cf. this vol., 33).—Accurate determination of F as CaF_2 is possible by using excess of CaCl_2 and centrifuging with the min. quantity of H_2O . Thus a solution containing about 0.4 g. of KF is evaporated to 5 c.c., 4 c.c. of half-saturated aq. CaCl_2 are added, and the mixture is centrifuged and decanted, boiled twice with 5 c.c. of saturated aq. CaF_2 , and centrifuged, and the process repeated four times with 5 c.c. of H_2O . The loss in 7 experiments varied from 0.15 to 0.95%, average 0.51%.

C. A. SILBERRAD.

Detection of minute amounts of sulphur dioxide. J. BOUGAULT and E. CATTELAÏN (Ann. Falsif, 1932, 25, 138—140).—Paper impregnated with 0.5% starch solution and dried at 30° is moistened with 1—2 drops of 0.1% KI (iodate-free) and coloured blue by suspension over 0.1*N*-I for 5—10 sec. Food products (wines, ketchup, sausages, etc.) are tested directly by acidifying with dil. H_3PO_4 20 c.c. or g. in a stoppered flask and suspending the blue paper from the stopper. Decolorisation is effected in 5 min. by as little as 0.00002 g. of SO_2 in 10 c.c.

H. R. JENSEN.

Standards for, and standard methods of analysing, sulphuric, hydrochloric, and nitric acids. E. S. PRSHEVALSKI, A. V. FROST, and T. N. KARSKAJA (Trans. Inst. Pure Chem. Reag. U.S.S.R., 1931, No. 12, 49—69).—Max. limits are given for the proportions of the different impurities allowed in "pure," "chemically pure," and "pure for analysis" H_2SO_4 , HCl, and HNO_3 . Methods are given for the determination of the impurities, and the results of analysis of many brands of each acid. In HCl 0.0002% and in HNO_3 0.0004% of SO_4^{2-} , in HNO_3 0.00003% and in H_2SO_4 0.0001% of Cl^- are detectable. For detecting HNO_3 in H_2SO_4 , the NHPh_2 reaction as described by Treadwell is suitable; for small proportions, the FeSO_4 reaction is better. Determination of Fe by the

thiocyanate method becomes more sensitive in presence of amyl alcohol. By Hefti's modification of the Gutzeit method, 0.000002% As may be detected in acids.

T. H. POPE.

Determination of sulphuric acid in presence of chromium salts by titration with alkali. B. I. LEONOV (J. Gen. Chem. Russ., 1931, 1, 1026—1034).—5 drops of 2% Na_2HPO_4 are added to the solution, containing H_2SO_4 and $\text{Cr}_2(\text{SO}_4)_3$, and 0.1*N*-NaOH is added to the appearance of the Tyndall effect due to separation of CrPO_4 . An error of $> 2\%$ is obtained when the $\text{Cr}_2(\text{SO}_4)_3$ content is > 2 g.

R. TRUSZKOWSKI.

Acidimetric determination of persulphates with and without catalysts. J. H. VAN DER MEULEN (Rec. trav. chim., 1932, 51, 445—451).—Solutions of persulphates are completely decomposed by boiling for 3—5 min. with excess of H_2O_2 , and the resulting MHSO_4 can be titrated with alkali. The reaction is accelerated by addition of AgNO_3 and/or MnSO_4 . The use of H_2O_2 entirely prevents oxidation of NH_3 when the NH_4^+ salt is used.

F. L. USHER.

Determination of ammonia without distillation. P. SORS (Chem.-Ztg., 1932, 56, 156).— NH_3 can be rapidly determined in solutions of NH_4 salts free from heavy metals by neutralisation with NaOH (Me-orange or *p*-nitrophenol), addition of a measured excess of NaOH, expulsion of the NH_3 by boiling, and titration of the excess NaOH.

A. R. POWELL.

Detection of nitrous oxides and iron in sulphuric acid. L. W. MARRISON.—See B., 1932, 419.

Micro-determination of phosphoric acid with strychnine molybdate. H. KLEINMANN (Mikrochem., 1932, 11, 139).—A reply to Rauterberg (this vol., 354).

F. L. USHER.

Reactions between certain metallic ions and ammonium aurintricarboxylate. J. H. YOE (J. Amer. Chem. Soc., 1932, 54, 1022—1023).—Reactions of As^{III} , Nb^{II} , Dy^{III} , Gd^{III} , Hf^{IV} , Ir^{IV} , Mo^{V} , Pr^{III} , Re , Rh^{III} , Ru^{III} , Sm^{III} , Ta^{V} , Te^{VI} , Tm^{III} , W^{VI} , $(\text{UO}_2)^{\text{II}}$, V^{II} , and Y^{III} with "aluminon" are described. None of these interferes with the detection of Al by the reagent.

R. H. CHERRY (c).

Titration of boric acid. J. C. KRANTZ, jun., and C. J. CARR (J. Amer. Pharm. Assoc., 1932, 21, 350—353).—Various methods of titration have been examined. The following modification of the U.S.P. method given by the Pacific Coast Borax Co. is the most accurate. A solution of 1.25 g. of boric acid in 25 c.c. of H_2O and 25 c.c. of glycerol (p_H of mixture 3.1) is titrated with *N*-NaOH, using phenolphthalein, and after the appearance of the pink colour this is discharged by the addition of a further 25 c.c. of glycerol (p_H of mixture 7.5) and the titration continued until the pink is restored (p_H 8.3). Theoretical results are obtained. The probable error of a single determination is 0.19%.

E. H. SHARPLES.

Use of fused sodium hydroxide in analytical chemistry. O. BRUNCK and R. HÖLTJE (Angew. Chem., 1932, 45, 331—334).—The technique of fusion with NaOH is discussed with special reference

to the analysis of silicates, TiO_2 , titanates, corundum, aluminates, bauxite, monazite, tungstates, chrome ironstone, W, W-rich alloys, and cassiterite.

E. S. HEDGES.

Determination of silica in volcanic tufa. A. STEPOE (Bul. Chim. pura appl., Bukarest, 1931, 33, 11—17; Chem. Zentr., 1932, i, 845).—Results of the determination of sol. SiO_2 by means of alkali depend on the dispersion, time, concn., etc.

A. A. ELDRIDGE.

Analysis of compounds containing silica and alumina. J. DELFORGE (Bull. Soc. chim. Belg., 1932, 41, 95—97; cf. B., 1931, 491).—A reply to criticisms by Delfeld (B., 1931, 1091). In the separation of Ti and Fe, it is advantageous to reduce the latter with H_2S rather than with SO_2 .

F. L. USHER.

Carbonate content of volumetric sodium hydroxide solutions. J. E. S. HAN and T. Y. CHAO (Ind. Eng. Chem. [Anal.], 1932, 4, 229—232).—The methods of freeing "oil lye" and volumetric NaOH solutions from Na_2CO_3 have been investigated by determining the minute amount of Na_2CO_3 left in the solutions after the addition of various precipitants. $Ba(OH)_2$ and Ba salts were found to be the best precipitants. The technique of Warder's differential titration method has been improved.

E. S. HEDGES.

Sensitive reaction for cyanates, especially in presence of cyanides. M. LINHARD and M. STEPHAN (Z. anal. Chem., 1932, 88, 16—23).—The solution containing CNO' in presence of CN' is pptd. with $AgNO_3$. The filtered and dried ppt. is suspended in Et_2O and cyclohexene added with sufficient I to colour it. The 2-iodocyclohexylcarbimide (I) formed may be recognised by its pungent odour and the fact that it forms with NH_3 a white, flocculent ppt. of (I) consisting of very fine crystals. If the amount of CNO' is very small the ppt. appears only after a few min. as fine colourless needles. The test is unaffected by most inorg. ions. In the presence of CN' ICN is formed and this also gives a pungent additive compound with cyclohexene, so that the ppt. with NH_3 is necessary for distinguishing CNO'. The sensitivity of the method in aq. solution is determined by the solubility of $AgCN$. 1 mg. of KCNO in 100 c.c. of H_2O gives no ppt. with $AgNO_3$, but 3 mg. give a turbidity which results in an easily recognisable ppt. of (I).

M. S. BURR.

Analysis of helium without the aid of liquid air. A. CHEREPENNIKOV (Prirodn. Gaz., 1931, 2, 83—90).—Charcoal cooled by means of solid CO_2 is employed.

CHEMICAL ABSTRACTS.

Indirect volumetric determination of sodium based on reduction and titration of uranium in magnesium sodium uranyl acetate. N. H. FURMAN, E. R. CALEY, and I. C. SCHOONOVER (J. Amer. Chem. Soc., 1932, 54, 1344—1349).—The $NaMg(UO_2)_3(OAc)_9 \cdot 6 \cdot 5H_2O$ is dissolved in 2% H_2SO_4 and reduced in a Jones reductor, then stirred for 5 min. while a rapid stream of air is passed through it to oxidise U^{III} to U^{IV} . After adding approx. 0.2N- $Ce(SO_4)_2$ and stirring vigorously for 5 min. the excess of $Ce(SO_4)_2$ is titrated potentiometrically with standard $FeSO_4$ solution. Instead of $Ce(SO_4)_2$, $KMnO_4$

can be used. 10 mg. or less of Na may be determined with an error of <0.1 mg. W. T. HALL (c).

Detection of beryllium in minerals. G. RIENACKER (Z. anal. Chem., 1932, 88, 29—38).—The sensitivity of Fischer's quinalizarin test for Be (A., 1927, 36; 1928, 385) has been confirmed. The test is unaffected by the presence of Al_2O_3 , SiO_2 , or TiO_2 , but Fe and Mg must be absent. Fe and Mg may be removed as hydroxides, without taking with them any adsorbed $Be(OH)_2$, by fusing the mineral with NaOH, dissolving out the beryllate by treatment with ice, filtering, and washing the residue of $Mg(OH)_2$, $Fe(OH)_3$, etc. The alkalinity of the filtrate is reduced to approx. 0.33N-NaOH by partial neutralisation with H_2SO_4 . A few drops of an alcoholic quinalizarin solution give the characteristic cornflower-blue coloration. A determination of the order of magnitude of the Be content may be obtained by diluting to the sensitivity limit. Direct colorimetric determination cannot be made. 0.01% Be may be recognised in 0.1 g. of mineral.

M. S. BURR.

Determination of beryllium. L. FRESSENIUS and M. FROMMES.—See B., 1932, 429.

Determination of beryllium in alloys. H. ECKSTEIN.—See B., 1932, 427.

Colour reactions for magnesium. N. A. TANANAEV (Z. anal. Chem., 1932, 88, 93—94).—Two colour reactions with test-papers are described, by one of which 0.006 mg. of Mg in 0.005 c.c. can be detected.

F. L. USHER.

Analysis of limestone. M. I. BLINOVA (Udobr. Urozhai, 1931, 3, 754—760).—Accurate results are obtained either by titration or by volumetric determination of CO_2 evolved. A modified Schübler calcimeter is described.

CHEMICAL ABSTRACTS.

Determination of calcium carbide in calcium cyanamide by means of cuprous acetylide. F. TROST.—See B., 1932, 420.

Determination of the hardness of water. J. LEICK.—See B., 1932, 450.

Determination of calcium, and its separation from magnesium by means of sodium tungstate. D. KATAKOUSINOS (Praktika, 1931, 4, 404; Chem. Zentr., 1932, i, 844).—Excess of Na_2WO_4 does not affect the result when the solution is hot, contains NH_4Cl , and is alkaline with NH_3 ; sufficient Na_2WO_4 must be added to make the reaction quant. The white ppt. is $CaWO_4$; the difference in wt. in two or more determinations is ± 0.004 g. A. A. ELDRIDGE.

Separation and determination of calcium and magnesium. 8-Hydroxyquinoline-saccharate method. A. C. SHEAD and R. K. VALLA (Ind. Eng. Chem. [Anal.], 1932, 4, 246).—Ca is pptd. as oxalate and Mg as the 8-hydroxyquinoline compound simultaneously. The mixed ppts. are ignited to the oxides and when in the freshly-ignited state are treated with 30% saccharate solution. CaO dissolves and MgO is insol.

E. S. HEDGES.

Determination of barium in ferriiferous minerals. E. CHAUVENET and P. AVRARD (Compt. rend., 1932, 194, 1164—1166).— CCl_4 is passed over the mineral (about 1 g.) at 450° ; after about 30 min.

all Al and most of the Fe are removed as AlCl_3 and FeCl_3 , which mostly dissolve in condensed CCl_4 ; a further 2 hr. is required to convert into chlorides Ca, Mg, most of the Mn, and Ba present as BaCO_3 with a little as BaSO_4 . These are dissolved out, leaving the silicates, SiO_2 , BaSO_4 , and a little Fe as oxychloride. The amount of chlorides in solution is insufficiently appreciable to dissolve the BaSO_4 . This residue is fused with alkali and extracted with HCl, and the residue again treated with CCl_4 , which removes the Fe and Al which were in the silicates, and chlorinates any Mn and some more Ba. From the residue the Fe oxychloride is removed by aqua regia, and the insol. portion (BaSO_4 and SiO_2) treated with aq. HF.

C. A. SILBERRAD.

Methyl-red as an adsorption indicator. G. BATCHELDER and V. W. MELOCHE (J. Amer. Chem. Soc., 1932, 54, 1319—1323; cf. A., 1931, 925).— Na_2SO_4 solution cannot be successfully titrated with BaCl_2 in presence of Me-red, for the change from yellow to red at the equiv. point is not sufficiently sharp. Before the equiv. point is reached, the BaSO_4 tends to adsorb SO_4^{--} , but as soon as a slight excess of Ba^{++} has been added, Ba^{++} ions are adsorbed and tend to drag down OH' rather than the negative dye ions, thus lowering the p_{H} .

W. T. HALL (c).

Determination of barium as chromate. LEMARCHANDS and SIROT (Compt. rend., 1932, 194, 1577—1579; cf. A., 1908, ii, 133; 1927, 223).—At 100° BaCrO_4 is sol. in H_2O to the extent of 11.81 mg. per litre, giving a solution $0.465 \times 10^{-4}N$. In aq. KCl as the concn. of KCl rises from 0.333N to 1.275N that of BaCrO_4 rises from $0.8415 \times 10^{-4}N$ to $9.73 \times 10^{-4}N$, giving for K ($=[\text{K}_2\text{CrO}_4][\text{BaCl}_2]/[\text{BaCrO}_4][\text{KCl}]$) 1.24×10^{-6} ; the activity coeff. of KCl falls from 1.08 for 0.333N to 0.873 for 1.275N.

C. A. SILBERRAD.

Determination of lead peroxide. III. A. V. PAMFILOV and (MISS) E. G. IVANČEVA (Z. anal. Chem., 1932, 88, 23—29).—Determination of PbO_2 by reducing with an alkaline solution of As_2O_3 and titrating the excess of As_2O_3 gives too high results. By using an acid solution of As_2O_3 and titrating the excess with NaBrO_3 , either by a simple potentiometric method or by the use of indicators such as indigo-carmin, the results approach in accuracy those obtained by the standard American method in which I is liberated from KI and titrated with $\text{Na}_2\text{S}_2\text{O}_3$, and the materials employed are considerably cheaper.

M. S. BURR.

Determination of lead in minerals. (Radioactive indicators in analytical chemistry.) G. VON HEVESY and R. HOBBIÉ (Z. anal. Chem., 1932, 88, 1—6).—Small quantities of Pb in minerals are determined by removing SiO_2 by HF, pptg. the sulphates, transforming into acetates, adding Ag_2SO_4 to both the acetate solution and the sulphate filtrate, pptg. Ag_2S and PbS together with H_2S , filtering, and dissolving in conc. HNO_3 . Sulphates are formed by oxidation and the solution is evaporated to dryness. The residue is dissolved in 0.001N- HNO_3 , carbamide added, and the solution electrolysed with an e.m.f. of 2 volts. PbO_2 is deposited on the Pt anode and weighed. Radioactive control of the completeness of the pptn. is exercised by adding a known quantity

of Ra-D before pptn. of the sulphides and comparing the activity of this with the activity of the final product, after correcting for the absorption of radiation by the PbO_2 deposit. If less Ra-D is pptd. than was originally added the deficiency represents the relative amount of Pb in the mineral which has not been deposited and a correction can be applied. The amount of pure PbO_2 present in the electrolytic deposit may be checked by a colorimetric method, using the reaction with $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$.

M. S. BURR.

Determination of small quantities of thallium in presence of lead and bismuth. F. PAVELKA and H. MORTH (Mikrochem., 1932, 11, 30—33).—When a solution of a Tl salt ($2-10 \times 10^{-5}$ g. per c.c. as Tl') is treated with excess of phosphomolybdic acid Pb and Bi form sol. compounds, whilst Tl forms a yellow hydrosol the turbidity of which is compared with that of a standard. K and NH_4 compounds must be absent.

F. L. USHER.

Argentometric determination of thallium. M. V. TROITZKI (J. Gen. Chem. Russ., 1931, 1, 1083—1085).—0.4 g. of Tl' salt (sol. or insol.) is treated with 50 c.c. of 0.1N- AgNO_3 , 5 c.c. of 2N-HCl, and 10 c.c. of 15% NaOH, and the mixture is heated during 30 min. at 100° in absence of light. It is then filtered, and the washed residue of Ag, AgCl, and $\text{Tl}(\text{OH})_3$ is treated with 2 c.c. of conc. HNO_3 at 100° , whereby Ag and $\text{Tl}(\text{OH})_3$ are dissolved. The solution is diluted to 50 c.c., and AgNO_3 is determined by titration with NH_4CNS , when the no. of c.c. of 0.1N- NH_4CNS multiplied by 0.01022 gives the Tl' content in g. For the micro-determination of Tl', 2 c.c. of solution, containing >5 mg. of Tl', are treated with 1 c.c. of 0.1N- AgNO_3 , 2 c.c. of 0.1N-HCl, and 1 c.c. of N-NaOH, and the mixture is treated further as in the macro-method, substituting centrifuging for filtration, and taking 3 drops of HNO_3 in place of 2 c.c. An accuracy of 99.3—100.16% is obtained with the macro- and of 98.7—103.1% with the micro-method.

R. TRUSZKOWSKI.

Determination of thallium, using hypiodite. M. V. TROITZKI (J. Gen. Chem. Russ., 1931, 1, 1086—1088).—A solution of 0.1—0.5 g. of Tl' salt in 20—30 c.c. of H_2O is mixed with 25 c.c. of 0.1N-I, and 15% NaOH is added until the solution has a light yellow colour, when it is diluted to 100 c.c. After 15 min., the solution is filtered, and I, liberated by addition of dil. HCl, is determined in 50 c.c. of the filtrate. The Tl' content is calc. according to the equation $\text{TlNO}_3 + 2\text{I} + 3\text{NaOH} \rightarrow \text{Tl}(\text{OH})_3 + \text{NaNO}_3 + 2\text{NaI}$.

R. TRUSZKOWSKI.

Determination of copper. Clarke and Jones' method. L. C. HURD and J. S. CHAMBERS (Ind. Eng. Chem. [Anal.], 1932, 4, 236—238).—The method (A., 1929, 900) is suitable only under carefully controlled conditions and is not recommended for general use. If the method is used, the prep. of a series of colour standards of KMnO_4 is suggested.

E. S. HEDGES.

Determination of copper in presence of iron with salicylaldoxime. W. REIF (Z. anal. Chem., 1932, 88, 38—40).—Practically the same method is used as in the micro-determination of Cu (A., 1931,

927), but, in order to prevent pptn. of Fe, tartaric acid is first added to the acid solution and then aq. NH_3 until the solution is green, due to the mixture of the blue ammoniacal Cu and the yellow Fe tartrate complex. Saturated aq. NH_4OAc is then added drop by drop until the green colour disappears. Salicylaldoxime solution, prepared by Ephraim's method (A., 1930, 1393), is added in slight excess, and, after leaving for 20–30 min., the ppt. is collected on a sintered glass plate, dried at 105° , and weighed as $(\text{C}_7\text{H}_6\text{O}_2\text{N})_2\text{Cu}$. M. S. BURR.

Electrolytic micro-determination of copper in ammoniacal solution. A. OKAČ (Z. anal. Chem., 1932, 88, 108–119).—The Cu compound, containing 0.2–5.0 mg. Cu, is dissolved in 6–7 c.c. of aq. NH_3 and electrolysed for 10 min. at 2 volts. A continuous stream of CO_2 keeps the liquid stirred and furnishes the necessary electrolyte. Examples of the method, which is rapid and accurate, are given.

F. L. USHER.

Electrolytic micro-determination of mercury. F. PATAT (Mikrochem., 1932, 11, 16–21).—A solution of a Hg salt in 0.1N- HNO_3 is electrolysed at 3 volts with a fine Au wire (0.1–0.15 g.) as cathode. 0.1–1.0 mg. of Hg can be determined. The cathode is weighed on a microbalance. The current (0.025 amp.) is passed for 20 hr. Org. acids should be absent. The method is accurate.

F. L. USHER.

Micrometric determination of minimal quantities of mercury. V. MAJER (Mikrochem., 1932, 11, 21–30).—Hg (10^{-7} – 1.4×10^{-5} g. in 5 c.c. of liquid) may be determined by deposition on a fine Fe wire in presence of KCl and CuSO_4 . A stream of CO_2 from a capillary keeps the liquid stirred and protects the metal from oxidation. Reduction is complete (99%) in $1\frac{1}{2}$ hr. The wire is subsequently heated and the Hg condensed in a fine capillary in which the globules are measured under a microscope. The Hg need not all be in a single globule.

F. L. USHER.

Determination of actinium in uranium minerals. (MLLE.) E. GLEDITSCH and E. FOYN (Compt. rend., 1932, 194, 1571–1572).—The Ac:U ratio has been determined (1) by extraction of Ac and (2) by pptn. of Pa with Ta, the radioactivities being measured with a Wulff electrometer. The ratios thus deduced from broeggerite (from Raade) average 2.7:100, and those from Cornish pitchblende 3.3:100, with a probable error $> 10\%$.

C. A. SILBERRAD.

Molecular spectra and spectroscopic analysis.

II. Analysis of lanthanum. G. PICCARDI and A. SBERNA (Atti R. Accad. Lincei, 1932, [vi], 15, 83–88).—La can be detected by an examination of the band spectra of LaO just as accurately as by the method of spark spectra; with small concn. and in presence of elements which give a complicated spectrum the method is more sensitive. Quantitatively, the accuracy is comparable with that obtainable by optical methods.

O. J. WALKER.

Micro-test for aluminium. F. L. HAHN (Mikrochem., 1932, 11, 33–36).—Filter-paper soaked in a $\text{C}_5\text{H}_5\text{N}$ solution of 1:2:5:8-tetrahydroxyanthraquinone and subsequently dried is coloured violet by NH_3 and brown by AcOH vapour, but a spot made

with a drop of solution of an Al salt remains unchanged. 5×10^{-7} g. of Al can be detected in this way. When the test is carried out in a test-tube, 2×10^{-8} g. can be detected. Mg present in excess does not interfere.

F. L. USHER.

Permanganate reaction of manganese and a technique permitting it in a strongly chlorinated medium such as sea-water. G. DENIGÈS (Bull. Soc. chim., 1932, [iv], 51, 380–384).—The reaction $\text{Mn}^{++} \rightarrow \text{MnO}_4'$ may be carried out conveniently by using H_2SO_4 and Bi peroxide. In the presence of halogens Mn^{++} may be determined as MnO_4' by adding conc. H_2SO_4 to the boiling solution, adding a drop of 5% AgNO_3 , and then $\text{K}_2\text{S}_2\text{O}_8$. The use of NaOCl with CuSO_4 as catalyst enables Mn^{++} to be determined colorimetrically as MnO_4' in the presence of several thousand times the wt. of Cl' .

E. S. HEDGES.

Chromous sulphate as reducing agent in the volumetric determination of iron. W. M. THORNTON, jun., and J. F. SADUSK, jun. (Ind. Eng. Chem. [Anal.], 1932, 4, 240–243).— CrSO_4 solutions which are suitable for analytical purposes can be prepared from $\text{K}_2\text{Cr}_2\text{O}_7$ by means of the Jones reductor. A solution of CrSO_4 containing $> 0.18\text{N-H}_2\text{SO}_4$ can be kept without appreciable change for 2 months if properly stored; it is unnecessary to remove the dissolved Zn. Fe^{+++} in cold solution can be determined by potentiometric titration with CrSO_4 in the presence of a small quantity of KCNS .

E. S. HEDGES.

Determination of iron and manganese in natural carbonates. S. V. POTANENKO.—See B., 1932, 382.

Permanganometric determination of cobalt. J. LEDRUT and L. HAUSS (Bull. Soc. chim. Belg., 1932, 41, 104–114).—Determination of Co by pptg. with $\text{Na}_2\text{C}_2\text{O}_4$ in AcOH solution leads to results about 20% too high. By working in 25% HCO_2H the error is only a few tenths %, as under these conditions the ppt. has a const. composition (CoC_2O_4) and is sol. to the extent of about 6 mg. Co per litre. NH_4' and NO_3' must be absent.

F. L. USHER.

Analysis of nickel by Parr and Lindgren's method. G. I. SMIRNOV (Uchen. Zapiski Kazan. Gosudarst. Univ., 1930, 90, No. 6, 1025–1035).—Parr and Lindgren's modification of the dimethylglyoxime method is more exact than other methods generally used.

CHEMICAL ABSTRACTS.

Electrometric titration of nickel in steel. W. BOHNHOLTZER.—See B., 1932, 430.

Colorimetric test for chromium. G. C. SPENCER (Ind. Eng. Chem. [Anal.], 1932, 4, 245–246).—Wool is dyed in 1% serichrome-blue R a bright crimson colour changed to navy-blue by immersion in $\text{H}_2\text{Cr}_2\text{O}_7$ solution. By preparing a series of colour standards the method may be used as an approx. method of determining small amounts of Cr. The reaction appears to be sp. for $\text{H}_2\text{Cr}_2\text{O}_7$.

E. S. HEDGES.

Test paper for molybdenum: application to the detection and rapid determination of molybdenum in steels. E. BERTRAND (Bull. Soc. chim. Belg., 1932, 41, 98–103).—Filter-paper is covered

with a thin layer of H_2WO_4 and a drop of the solution (acidified) to be tested is placed on it. On adding $SnCl_2$ in aq. HCl a greyish-blue stain, surrounded by a colourless ring, is produced if Mo is present, and the intensity and time of appearance can be used for the determination of Mo. 0.00005 mg. of Mo in a drop of solution can be detected. F. L. USHER.

Determination of molybdenum with potassium permanganate. E. CARRIÈRE and R. LAUTIÉ (Compt. rend., 1932, 194, 1167—1168, 1284).—When K_2MoO_4 (0.5 g.) dissolved in 150 c.c. of 18% aq. H_2SO_4 is reduced at 50—60° by 15 g. Zn as wire (any other form gives unsatisfactory results, as also does HCl in place of H_2SO_4), a salt of Mo_2O_3 or MoO_3 itself is obtained, and an arrest in the reduction occurs at the point corresponding with its formation. As soon as reduction is complete work must be carried on in CO_2 (cf. A., 1929, 165). C. A. SILBERRAD.

Determination of tin in stannic oxide and cassiterite by means of reducing vapours. G. L. CHABORSKI and M. N. BADESCU (Bul. Chim. pura appl., Bukarest, 1932, 32, 7—18; Chem. Zentr., 1932, i, 554).—Sn is determined by observing the difference in wt. when EtOH vapour is passed over SnO_2 for 5—10 min. at a high temp.; SnO_2 is reduced to Sn. A. A. ELDRIDGE.

Volumetric determination of tin. Application to the separation of antimony and tin. P. E. WINKLER (Bull. Soc. chim. Belg., 1932, 41, 115—137).— SnS_2 is dissolved in NaOH, neutralised with HCl, and Zn is added. The pptd. Sn is dissolved with excess of Zn in HCl, the H_2 liberated providing a reducing atm., and the solution obtained is titrated with I and $Na_2S_2O_3$. In the separation of Sb and Sn by the $H_2C_2O_4$ method, the Sn may be recovered quantitatively from the filtrate by removing the $H_2C_2O_4$ with $HClO_3$ and HCl. The result is uniformly slightly low, but a systematic correction may be made. E. S. HEDGES.

Determination of small quantities of vanadium in soils and rocks with *p*-phenylenediamine hydrochloride. D. KATAKOUSINOS (Praktika, 1931, 4, 448—451; Chem. Zentr., 1932, i, 845).—Dark-coloured complexes formed on addition of conc. solutions of *p*-phenylenediamine to cold solutions of V salts contain 37.72—37.80% V_2O_5 ; in dil. solution colours between yellow and dark green are produced. 0.005 mg. V in 10 c.c. H_2O can be detected. The colour in neutral solution is yellow, in HCl solution pink to red. A. A. ELDRIDGE.

Analytical chemistry of tantalum, niobium, and their mineral associates. XXII. Separation of the earth acids from metals of the hydrogen sulphide group. E. F. WATERHOUSE and W. R. SCHOELLER (Analyst, 1932, 57, 284—289).—If the authors' method (this vol., 36) is extended to the separation of Ta and Nb from Sb, Bi, and Cu, it is found that treatment with H_2S at 60° of a solution of the H sulphate fusion in tartaric acid gives a ppt. which always contains a few mg. of earth acid owing to hydrolysis of the tartaric-earth acid complexes. On pouring a warm solution of this ppt. in conc. H_2SO_4 , to which 20% tartaric acid and excess

of NH_3 have been added, into fresh $(NH_4)_2S$, Bi and Cu are pptd. as sulphides, and after filtration the Sb may be obtained by acidification with AcOH and titrated with $KMnO_4$. The final filtrate contains the contaminating earth acids, which are pptd. in the usual way (*loc. cit.*) and added to the ppt. from the tartaric hydrolysis of the first filtrate. The errors for 0.1—0.25 g. of earth acid are usually <1 mg. of earth acid, Sb_2O_3 , Bi_2O_3 , or CuO. J. GRANT.

Analytical application of catalytic reactions. F. FEIGL and E. FRÄNKEL (Ber., 1932, 65, [B], 539—546).—Pd is detected by pptn. of Ni from solutions of $Ni(OAc)_2$ and NaH_2PO_2 , the limit of concn. being 1 in 4×10^8 ; Pt, Os, and Ru (1 in 6.6×10^6 , 2×10^7 , and 2×10^7 , respectively) behave similarly (possibly owing to presence of Pd), whereas Rh is inactive. The oxidation of $Mn(OH)_2$ to $NaMnO_4$ by NaOBr is catalysed by Ni^{++} and Co^{++} in addition to Cu^{++} . Mn (1 in 20×10^6) is detected by the formation of $KMnO_4$ by the action of $KBrO_3$ and KBr in alkaline solution in presence of $CuSO_4$; if Co or Ni is also present, more $CuSO_4$ must be added. Alkali hypobromite solutions are decomposed in presence of Cu, Co, or Ni, but not of Bi, Pb, Cd, Fe, Mn, or Ba; in presence of $MnSO_4$ the decomposing action of $CuSO_4$ is enhanced. Ag (1 in 12×10^4 or 1 in 10^6) is detected by its ability to catalyse the reduction and consequent decolorisation of brown Mn^{+++} or Mn^{++++} solutions in 2.5*N*-HCl or Ce^{+++} solutions in dil. HNO_3 ; the reaction is applicable to mixtures of AgCl, $PbCl_2$, and Hg_2Cl_2 from which the Hg_2Cl_2 has been removed by gentle ignition. SO_2 (1 in 125,000) is detected by the induced oxidation of $Ni(OH)_2$ to Ni_2O_3 and identification of the latter by the blue colour with benzidine acetate solution. H. WREN.

High-precision constant-temperature bath. A. L. FERGUSON, K. VAN LENTE, and R. HITCHENS (Ind. Eng. Chem. [Anal.], 1932, 4, 218—219).—The bath is fitted with a special relay and a Hg-steel regulator, maintains a const. temp. to within 0.01° for periods of several months, and can be kept const. to within 0.001° for shorter intervals. The liquid used in the bath is "petrolatum" and freedom from all the usual disturbances is claimed.

E. S. HEDGES.
Thermostatic control operated by ordinary alternating current. J. B. RAMSEY and T. A. WATSON (Ind. Eng. Chem. [Anal.], 1932, 4, 164—165).—A circuit breaker operated by a.c. is described. The thermoregulator requires an inert atm. of the electrical contact in order to obviate fouling.

E. S. HEDGES.
Double-tube combustion furnace. C. B. DE WITT (Ind. Eng. Chem. [Anal.], 1932, 4, 225—226).—The furnace is designed for org. analysis. It has two combustion tubes, the temp. of each of which can be regulated at will without affecting the other; it dispenses with clay tiles and radiates less heat into the room.

E. S. HEDGES.
Laboratory furnace for high temperatures. H. S. BOOTH and R. WARD (Ind. Eng. Chem. [Anal.], 1932, 4, 199—200).—An electrically heated furnace, giving a temp. const. to $\pm 5^\circ$ between 1000° and 1500°, is described. E. S. HEDGES.

Improvised micro-burner. LUDY, jun. (Pharm. Zentr., 1932, 73, 209—210).—A burner suitable for micro-sublimations is described.

N. H. HARTSHORNE.

Errors in thermal measurements. J. R. PARTINGTON (Nature, 1932, 129, 615—616).—Attention is directed to the neglect of the errors involved in the use of metal wire thermometers.

L. S. THEOBALD.

Method of regulating a water-bath to different fixed temperatures in succession. A. BECKEL (Chem.-Ztg., 1932, 56, 331—332).—The temp. of a H₂O-bath can be regulated to $\pm 0.1^\circ$ by means of hot and cold H₂O feeds controlled by screw pinch-cocks with indicators attached for fine adjustment. The temp. of the hot H₂O is controlled by a heating spiral or screened gas flame and the two supplies are mixed before they enter the H₂O-bath. The pressure head is regulated by open tanks in the feed.

C. IRWIN.

Apparatus for determination of m. p. M. MATSUI and H. KATO (J. Soc. Chem. Ind. Japan, 1932, 35, 168—171b).—A bar of Au-plated Cu has a groove 1 mm. deep on the upper surface, an electric heater at one end, and Cu and constantan wires fixed to the side forming a thermocouple. The substance is placed in the groove; the sharp line dividing the melted from the unmelted surface travels along the bar, and as it passes the thermocouple the reading is taken. A Leeds-Northrup potentiometer is used.

C. IRWIN.

Determination of m. p. of small volatile crystals. Detection of diacetyl in pyrogenic gases from sugars and sugar-like substances. H. SCHMALFUSS and H. BARTHEMEYER [with H. SCHAARE] (Mikrochem., 1932, 11, 6—16).—A method of manipulating very small quantities of volatile cryst. ppts. is described. Ac₂ has been identified by the m. p. of its dioxime among products of the pyrogenic decomp. of sucrose, glucose, starch, cellulose, and tartaric acid.

F. L. USHER.

Infra-red spectrometer of large aperture. H. M. RANDALL (Rev. Sci. Instr., 1932, [ii], 3, 196—200).—An instrument for use from 50 to 300 μ is described. The parabolic concave mirror used is 24 in. in diameter and fills a grating 10 \times 22 in.

C. W. GIBBY.

Large grating spectrograph. A. L. LOOMIS and G. B. KISTIAKOWSKY (Rev. Sci. Instr., 1932, [ii], 3, 201—205).—Improvements consist in a rigid grating mounting and a const.-temp. attachment.

C. W. GIBBY.

Recording apparatus for potentiometric determinations. P. DUBOIS (Compt. rend., 1932, 194, 1162—1164).—The solution under examination is placed in a revolving beaker, in which is fixed a SiO₂ tube containing an electrical resistance, which serves as a stirrer and to regulate the temp. The progress of the reaction is measured electrically by means of a standard electrode and another in the solution. The reagent is added from a burette attached to a balance to the knife-edge support of which is attached a mirror. The record is made by light reflected from this and the mirror of the galvanometer

connected with the two electrodes. The device has been used to determine Mn.

C. A. SILBERRAD.

Continuous measurement of p_H with quinhydrone electrodes. II. C. C. COONS (Ind. Eng. Chem. [Anal.], 1932, 4, 175—178).—An improved apparatus for continuous p_H measurement gives an error not exceeding $\pm 0.05 p_H$ between p_H 0 and 7.5. The error reaches ± 0.1 at p_H 8 and ± 0.2 at p_H 9. The time lag of the apparatus is negligible for most industrial applications, but may cause an error of $\pm 0.2 p_H$.

E. S. HEDGES.

Measurement of electromotive force by means of a valve null instrument and telephone. W. HILTNER (Chem.-Ztg., 1932, 56, 352).—A sensitive compensation method is described.

E. S. HEDGES.

Slotted watch glasses for use in electroanalysis. E. R. CALEY (Ind. Eng. Chem. [Anal.], 1932, 4, 223—224).—A watch glass having a radial slot cut by means of a thin carborundum wheel serves to prevent loss by spraying during electro-analytical determinations, whilst obviating the necessity of disconnecting the electrodes when the watch glass is removed or replaced.

E. S. HEDGES.

Measurement of the internal resistance of an accumulator, and of electrolytic resistances in general. E. DENINA and A. FRATES (Energia Elett., 1931, 8, 4 pp.; Chem. Zentr., 1932, i, 559).

Platinum resistance thermometry. III. Determination of low-temperature scale between 0° and -190°. S. KAMBARA and M. MATSUI (J. Soc. Chem. Ind. Japan, 1932, 35, 165—168b).—The equation $R_t = R [1 + At + Bt^2 + C(t - 100)t^3]$ is chosen and the fixed points selected for calibration are the b. p. of liquid O₂ and the m. p. of Hg. Trustworthy results for the former could be obtained only after long-continued annealing of the bulbs at 400° with cooling to the b. p. of liquid air. An attempt to use the sublimation point of solid CO₂ in a Dewar flask with 3 compartments, the outer ones filled with the solid CO₂ and the centre one containing the bulb and the stirrer, was unsuccessful. The m. p. of Hg was determined by melting frozen Hg slowly with ice and the results were checked with the equations for the bulbs obtained from the b. p. of O₂.

C. IRWIN.

Apparatus for electro dialysis. E. J. KING (Ind. Eng. Chem. [Anal.], 1932, 4, 201—202).—The colloidal solution is placed in a large dialysing thimble and in it is immersed a smaller dialysing thimble through which distilled H₂O flows. The larger thimble is immersed in a beaker containing flowing, distilled H₂O. A Pt electrode is placed in the inner thimble and the other electrode is a layer of Hg at the bottom of the beaker.

E. S. HEDGES.

Apparatus for calibration of flowmeters. G. W. SMITH (Ind. Eng. Chem. [Anal.], 1932, 4, 224—245).—An apparatus and procedure for calibrating flowmeters of the resistance-tube type for use with low rates of gas flow are described.

E. S. HEDGES.

Multiple-range flowmeters. S. YUSTER (Ind. Eng. Chem. [Anal.], 1932, 4, 224).—Two forms of

apparatus for the study of gaseous reactions by flow methods are described. E. S. HEDGES.

Purification of materials by vacuum distillation. E. W. FLOSDORF and A. E. PALMER (*J. Rheology*, 1932, 3, 205).—A distillation flask with two side-arms enables two fractions to be collected without interrupting the process. E. S. HEDGES.

Anti-foam still-head. C. W. EDDY (*Ind. Eng. Chem. [Anal.]*, 1932, 4, 198—199).—Two forms of apparatus for use at low pressures are described.

E. S. HEDGES.

Determination of specific gravity. W. NORMANN (*Chem.-Ztg.*, 1932, 56, 297; cf. *B.*, 1931, 399).—The method of suspending and weighing the apparatus formerly described is explained.

E. S. HEDGES.

Measurement of dissolution of metals in salt solutions. L. WHITBY (*Trans. Faraday Soc.*, 1932, 28, 474—478; cf. *A.*, 1928, 1333).—An apparatus is described for following accurately the course of the corrosion of metals by periodic determinations of the H_2 and O_2 in the gas enclosed over the corroding liquid. O_2 is not absorbed appreciably during the dissolution of Mg in 0.0001*N*- and 0.001*N*-NaCl.

J. G. A. GRIFFITHS.

Apparatus for quantitative catalytic reduction. H. PAGET and W. SOLOMON (*J.C.S.*, 1932, 1198—1200).—Two forms of apparatus (for use at atm. pressure and at high pressures, respectively), which enable the amount of absorbed gas to be determined accurately, are described.

E. S. HEDGES.

Gas absorption pipette. H. TRAMM (*Brennstoff-Chem.*, 1932, 13, 146—147).—The pipette consists of three bulbs. The upper bulb is packed with glass beads. The intermediate bulb is connected with the larger lower bulb directly by a short capillary tube and also by a wider tube joining the top of the former to the bottom of the latter. The lower bulb may also be packed with beads. When the gas is drawn into the pipette it passes through the upper bulb and thence by way of the wide connecting tube to the lower bulb, and is subjected therein to the action of the stream of absorbing liquid which flows from the intermediate bulb through the capillary tube.

A. B. MANNING.

Apparatus for dispersoid analysis. H. LEHMANN (*Chem. Fabr.*, 1932, 149—150).—A pipette apparatus for determining the concn. of suspensions is described.

E. S. HEDGES.

Soxhlet apparatus for large amounts [of material]. F. N. SCHULZ (*Biochem. Z.*, 1932, 247, 474—475).—The apparatus is made mainly of metal (Sn plate, Cu, Ni) with linen or silk as filtering medium.

W. MCCARTNEY.

Apparatus for micro-extraction on Soxhlet's principle. A. WASITZKY (*Mikrochem.*, 1932, 11, 1—6).—A simple glass extraction apparatus for dealing with about 1 g. of material, and suitable for use at atm. or reduced pressure, is described.

F. L. USHER.

Extraction apparatus and its use in quantitative analysis. G. THOMIS (*Praktika*, 1931, 6, 248—251; *Chem. Zentr.*, 1932, i, 552).

Extraction apparatus for solids. H. WOLLENBERG (*Chem.-Ztg.*, 56, 1932, 332).—The material to be extracted rests on a filter plate beneath which a centrally placed horizontal paddle revolves in the extracting liquid. The latter is forced up through the central part of the solid and downward through the periphery.

C. IRWIN.

Impervious crucibles of magnesium oxide. P. S. ROLLER and D. RITTENBERG (*Ind. Eng. Chem.*, 1932, 24, 436—440).—The refractory powder, which must pass a 200-mesh sieve and have appropriate distribution of particle size, is moistened with dil. HCl and H_3PO_4 and pressed in two stages in such a manner that the base is welded to the walls and a structure of uniform density is obtained. The dried crucible is fired in a high-frequency induction furnace with a graphite inductor at 2600°, the time during which it is above 1800° being min. The crucible is translucent and retains molten slags (at 1500°) for long periods although slow dissolution of the MgO may occur.

J. G. A. GRIFFITHS.

Laboratory ball mill. R. BLOCK and C. ROSETTI (*Chem.-Ztg.*, 1932, 56, 196).—The mill comprises a porcelain or Fe jar containing pebbles or steel balls and closed with a clamped-on lid; the jar is rotated at 300 rev. per min. on a horizontal circular table with an eccentric drive so that the balls and material to be ground are thrown about vigorously by the centrifugal action combined with the eccentric motion.

A. R. POWELL.

Characteristics of porous plates. H. RUDOLPH (*Chem. Fabr.*, 1932, 137—140).—Porous plates are made by binding grains (diatomaceous earth, etc.) with a suitable medium, the size of grains used determining the size of the pores. They are used for filtration, as diaphragms for surface combustion, etc. The "pore no." is the no. of pores per sq. cm., the porosity is the percentage of pore vol. to total vol. Microscopic examination can be carried out only by reflected light. Indirect tests of filter plates include the determination of the quantity of H_2O passed under given conditions, a test which is subject to numerous errors unless pressure, thickness of plate, temp., and purity of H_2O are all standardised. Similar errors arise in the determination of rate of transmission of air, but the difficulties are not so great. The transmission of air alone does not offer the same problem as the passage of air in counter-current to a solution through which the air or gas is bubbled.

C. IRWIN.

Filling device for upward-flow viscosimeters. W. G. BURRSTON (*Analyst*, 1932, 57, 309).—The level of liquid in a viscosimeter is adjusted rapidly and accurately, and the risk of fouling the walls above the lower reference mark is avoided, by the use of a T-piece fitted to the air-outlet end, one arm of which leads to a cock and the other to a levelling tube of the eudiometer type.

J. GRANT.

Approximate calibration of apparatus for measuring absolute viscosity. C. H. WEISS and M. LOUIS (*J. Rheology*, 1932, 3, 217—220).—Sources of error are discussed.

E. S. HEDGES.

Speed regulator for small laboratory motors. A. TIAN (*Bull. Soc. chim.*, 1932, [iv], 51, 419—420).—

A rubber disc is affixed. During rotation its radius increases until the periphery touches a suitably placed object, thus providing a limiting max. speed.

E. S. HEDGES.

Use of sand in centrifuging precipitates. S. STENE (Mikrochem., 1932, 11, 131—132).—Admixture of sand when centrifuging a ppt. prevents the latter becoming too firmly consolidated, and from being stirred up when the centrifuge is stopped.

F. L. USHER.

Hair-type humidity control. M. C. MARSH (J. Sci. Instr., 1932, 9, 153—157).—Hairs extended vertically are pulled sideways by springs, and operate relays which control the humidifying or drying apparatus.

C. W. GIBBY.

Simplified method of calculating tangents by theory of least squares. F. T. GUCKER, jun. and H. J. BRENNEN (J. Amer. Chem. Soc., 1932, 54, 886—888).—By choosing equally spaced positive and negative vals. of the independent variable and making the y -axis pass through the point at which the tangent is desired, $dy/dx = \Sigma xy / \Sigma x^2$. R. H. CHERRY (c).

Albertus Magnus as chemist. F. PANETH (Nature, 1932, 129, 613).—A criticism.

L. S. THEOBALD.

Early history of platinum. E. P. C. MEYER (Science, 1932, 75, 438).—References to Pt dated 1735 have been found. Earlier references are probable.

L. S. THEOBALD.

Geochemistry.

Upper air temperatures and humidities in the Indian Peninsula. K. R. RAMANATHAN and K. P. RAMAKRISHNAN (Nature, 1932, 129, 615).

L. S. THEOBALD.

Phosphate, nitrate, and nitrite in the sea-water of regions adjacent to Cape Cod. N. W. RAKESTRAW (Science, 1932, 75, 417—418).—Data are recorded graphically.

L. S. THEOBALD.

Reducing power of sea-water. P. CHAUCHARD (Compt. rend., 1932, 194, 1256—1259).—Defining reducing power as the no. of c.c. of $M/300\text{-KMnO}_4$ reduced by 1 litre rendered alkaline, the reducing power of sea-water off Brest in fine weather (with E. wind) was 12—15, in stormy weather (W. wind) 16—24. After a long period of stormy weather several days of calm are required to diminish the reducing power. In calm weather the power is nearly const. to 100 m. depth, and then diminishes rapidly.

C. A. SILBERRAD.

Organic carbon content of various waters. PICON (Compt. rend., 1932, 194, 1175—1177).—The C content of 15 different waters was determined. Very little difference was found in the case of waters from rivers, wells, and springs, but water treated with hypochlorite showed markedly less, that from a forest pond markedly more, C. No relation was traceable between the amounts thus found and results with KMnO_4 .

C. A. SILBERRAD.

Iodine content of some waters of S.E. Dakota. C. B. STONE (Proc. S. Dakota Acad. Sci., 1927, 10, [xxvii], 35—45).—The I content is low.

CHEMICAL ABSTRACTS.

Occurrence of iodine. E. SCHANTL (Chem.-Ztg., 1932, 56, 341—342).—The H_2O pumped from deep wells (about 400 m.) in certain localities in the East Indies contains considerable quantities of KCl, NaCl, CaCl_2 , and MgCl_2 and about 0.015% of MgI_2 . Methods in use for extracting the I are described.

E. S. HEDGES.

Radioactivity of the sulphuretted water at Thuès les Bains. E. CANALS (J. Pharm. Chim., 1932, [viii], 15, 397—400).—The radioactivities of the H_2O from several springs lie between 68×10^{-2} and 9.4×10^{-2} microcuries. There is no apparent relation

between the radioactivity and the chemical composition of the H_2O .

A. LAWSON.

Nitrogenous compounds and phosphate in the lake waters of Japan. S. YOSHIMURA (Proc. Imp. Acad., Tokyo, 1932, 8, 94—97).—Samples from about 80 Japanese lakes have been examined for free NH_3 , albuminoid NH_3 , NO_2' and NO_3' , sol. and total PO_4''' by colorimetric methods. Total N and PO_4''' are closely correlated in the different lake types.

W. R. ANGUS.

Spontaneous combustion in the marshes of Southern Louisiana. P. VIOSCA, jun. (Science, 1932, 75, 461—462).—Spontaneous ignition of the soil of a dried marsh is recorded.

L. S. THEOBALD.

New lime-precipitating bacterium from the Sevan Lake (Goktscha), *B. Sewanense*, spec. nov. P. KALANTARIAN and A. PETROSSIAN (Zentr. Bakt. Par., 1932, II, 85, 431—436).—The organism causes the pptn. of CaCO_3 as fine calcite crystals. No gas formation from sugars, starch, inulin, etc. occurs.

A. G. POLLARD.

Natural gases in Russia. G. A. SARKISYANTZ (Prirodn. Gaz., 1931, 2, 129—138).—Surakhani: CO_2 15—30, CH_4 75—79.5, C_2H_6 2—4, C_3H_8 and higher homologues 1.5—2%; gasoline 0.37—0.55 gallon per 1000 cu. ft. of gas. Bibi-Eibat: CO_2 4—8, CH_4 84—91, C_2H_6 2—4, C_3H_8 and higher homologues 3—4% (gasoline 0.77—1.00). Kirmaki: CO_2 4, CH_4 90—93, C_2H_6 2, C_3H_8 < 1% (gasoline 0.074—0.11). New Grozni: CO_2 trace, CH_4 18.3, C_3H_8 16.3, C_4H_{10} 27.8, C_5H_{12} and higher homologues > 31%. Old Grozni: CH_4 40, C_2H_6 7.08, C_3H_8 20.2, C_4H_{10} 18.4, C_5H_{12} and higher homologues > 13.6%. Maikop: CH_4 49, C_2H_6 13, C_3H_8 13, C_4H_{10} 7, C_5H_{12} and higher homologues > 8% (gasoline up to 12%).

CHEMICAL ABSTRACTS.

Radium and helium in petroleum beds. K. KREJCI-GRAF (Petroleum, 1932, 28, 12—14).—Contrary to a previous opinion (Salomon-Calvi, A., 1931, 1145), the Ra content of oil-bed waters is due to leaching alone. The reason for the comparative freedom from Ra of ordinary waters is that they contain SO_4'' ions. The storing of Ra and U in

organisms is shown to be probably without oleogeological significance. The He is derived from the disintegration of Em, which, being very sol. in petroleum, is conc. in it. N. H. HARTSHORNE.

Geochemistry of noble gases and radioactivity. V. G. CHLOPIN (Prirodn. Gaz., 1931, 2, 61—82).—Owing to the stability of He its accumulation in subterranean strata is governed by the total amount of radioactive elements.

CHEMICAL ABSTRACTS.

Escape of gas in sediments. H. KORN (Chem. Erde, 1932, 7, 1—23).—The decomp. of animal and vegetable remains in marine sediments may under certain conditions give rise to the generation of gases (H_2 , CH_4 , CO_2 , H_2S , NH_3) in considerable amounts. These gases may produce a porous texture in the rock or they may escape along channels. Examples are given of these channels in rocks, which have been described as fossil algae, worm tracks, and other problematical fossils. L. J. SPENCER.

Permian yellow sands of N.E. England. M. B. HODGE (Proc. Univ. Durham Phil. Soc., 1932, 8, 410—458).—Mechanical and mineralogical analyses of sands in Northumberland and Durham are given. C. W. GIBBY.

Formation of flint. H. DOUVILLE (Compt. rend., 1932, 194, 1285—1289).—The SiO_2 of sedimentary deposits arises from the spicules of sponges, tests of *Radiolaria*, etc. and is thus produced as micelles regularly grouped in a protoplasmic medium. On decay of the organisms these micelles move with Brownian motion in the resultant muddy slime, gradually uniting to form a gel, which then slowly passes into cryptocryst. chaledony where it replaces chalky deposits, and into cryst. fibrous chaledony or even quartz in empty spaces. In this way is explained the formation of the chalk flints and their occasional geodes without assuming complete dissolution of SiO_2 . C. A. SILBERRAD.

Veszelyite from Vaskö (Moravia). V. ZSIVNY (Z. Krist., 1932, 82, 87—110).—Veszelyite is monoclinic, $a : b : c = 0.7288 : 1 : 0.9542$, $\beta 76^\circ 37'$, hardness 4, no cleavage, slightly pleochroic, blue and greenish-blue; $d_{10}^{20} 3.34_3$; analysis CuO 37.82, ZnO 26.69, PbO 0.05, FeO 0.06, NiO trace, P_2O_5 18.43, H_2O 16.87%, corresponding with $(Cu,Zn)_3(PO_4)_2 \cdot 3(CuZn)(OH)_2 \cdot 4H_2O$, a formula applying equally to veszelyite from Broken Hill, to the isomorphous arakawite, and probably also to kipushite, the differences depending on the relative amounts of Cu and Zn (cf. A., 1875, 546; 1881, 368). C. A. SILBERRAD.

Narsarsukite. B. GOSSNER and H. STRUNZ (Z. Krist., 1932, 82, 150—151).—Narsarsukite consists of $1.027SiO_2 + 0.1707TiO_2 + 0.0394Fe_2O_3 + 0.0027Al_2O_3 + 0.006MgO + 0.006MnO + 0.260Na_2O + 0.0374F + 0.016H_2O$, and is composed of a mixture of $Na_2Ti(Si_4O_{11})$, $Na_2Fe(Si_4O_{10}F)$, and a little $Na_2(Mg,Mn)(Si_4O_9F_2)$, all three being isomorphous. It is tetragonal with $a 10.78$, $c 7.99$ Å., space-group probably C_{4h}^2 , perhaps C_{4h}^3 . C. A. SILBERRAD.

Hessite. L. TOKODY (Z. Krist., 1932, 82, 154—157).—Hessite from Botes (Hungary) contains Ag

59.41, Au 4.73, Te 35.97%, Fe trace; Sb, S, and SiO_2 are absent; $d^{20} 8.350$. It is probably monoclinic, the unit cell having $a 5.98$, $b 6.31$, $c 5.56$ Å., $\beta 75^\circ 2'$, and containing 3 mols. (Ag_2Te), one of which must differ in some way from the other two.

C. A. SILBERRAD.

Geochemistry of gallium. V. M. GOLDSCHMIDT and C. PETERS (Nachr. Ges. Wiss. Göttingen, 1931, 165—183; Chem. Zentr., 1932, i, 513).—The Ga content of many rocks and minerals has been determined, the arc spectrographic method being employed for quantities up to 0.01%. In the lithosphere Ga always accompanies Al, but the quant. relationship is not const. The at. ratio Ga : Al in the rocks of the lithosphere is $1 : 4-2 \times 10^4$. Ga occurs also in Fe meteorites and in technical Fe.

A. A. ELDRIDGE.

"Alkanasul," a new aluminium-bearing Chilean mineral. J. WESTMAN (Bol. min. Soc. Nac. Min., 1931, 43, 433—434; Chem. Zentr., 1932, i, 573).—The mineral, $d 2.90$, contains Al_2O_3 30.35, K_2O 5.61, Na_2O 3.70, SO_3 37.95, H_2O 16.11, Fe_2O_3 1.20, SiO_2 4.98%. On moderate roasting $Al_2(SO_4)_3$, K_2SO_4 , and Na_2SO_4 are obtained; heating at a higher temp., followed by extraction with H_2O , leaves a residue containing about 95% Al_2O_3 .

A. A. ELDRIDGE.

Genesis of oölites of Lorraine and Luxemburg. J. P. AREND (Compt. rend., 1932, 194, 1172—1175; cf. this vol., 493).—The origin of the Fe is discussed and an explanation of the formation of the "colloidal solid suspension" (this vol., 360) is offered.

C. A. SILBERRAD.

Spectrographic study of rocks and minerals of Katzenbuckel Mtn., Odenwald. F. SCHRÖDER (Neues Jahrb. Min., 1931, A, 63, 215—266; Chem. Zentr., 1932, i, 206).—The following elements are present in the minerals: Rb, Cu, (Au), (Be), Sr, Ba, Zn, Cd, rare earths, Ca, (In), Tl, Th, Sc, Sn, Pb, V, Mo, Cr, Mn, Co, Ni. The distribution of the elements is discussed. A. A. ELDRIDGE.

Structural formula of hydromagnesite. G. R. LEVI and D. GHIRON (Gazzetta, 1932, 62, 218—220).—In four typical hydromagnesites from various localities (Val d'Aosta, Texas, and Eubea) the ratio $MgO : CO_2$ is very nearly 4 : 3 and not 5 : 4 (cf. A., 1930, 435). O. J. WALKER.

Age of a monazite crystal from Portland, Connecticut. C. N. FENNER (Amer. J. Sci., 1932, [v], 23, 327—333).—Analysis gave Th 7.489, Pb 0.1007%; U absent. On the supposition that the Pb was derived from the Th by radioactive disintegration, this gives the age to be 2779×10^6 years, in good agreement with the age calc. from the analysis of a sample of uraninite from the same quarry (U.S. Geol. Survey Bull., 1889—1890, No. 78, 43).

N. H. HARTSHORNE.

Isomorphism of feldspars. E. SCHIEBOLD (Neues Jahrb. Min., 1931, A, 64, Bl.-Bd., 251—319; Chem. Zentr., 1932, i, 35—36).—A discussion.

A. A. ELDRIDGE.

Metallographic investigation of native silver. (SIR) H. C. H. CARPENTER and M. S. FISHER (Bull. Inst. Min. Met., 1932, No. 330, 22 pp.).—From micro-

graphic examination and heat-treatment tests on numerous samples of native Ag from 14 localities it is concluded that in the course of geologic ages native Ag may recrystallise at room temp. although the process is usually imperfect and localised. In deposits formed at a low temp., and never subjected to heat, some at least of the Ag retains its original structure, whilst that which has recryst. has not a uniform homogeneous structure like that of Ag recryst. by heat. Conversely, when native Ag has a homogeneous recryst. structure it may be assumed that the Ag was deposited at a high temp. or has subsequently been metamorphosed by heat. Native Ag from most localities has been deposited by meteoric waters or by cool hypogene solutions, but that found in N. Rhodesia, at Lake Superior, and in the Cobalt district has been deposited by hot juvenile solutions at above 200°. Both Ag and Cu at Lake Superior have been deposited at 200—250°. A natural alloy from Cobalt contained Ag 85.6, Sb 12.1, As 0.6, and Bi 1.2% and had a duplex Widmanstätten structure; it had probably been deposited from hot hypogene solutions as a homogeneous solid solution from which a second phase was subsequently pptd. to give the characteristic structure. Attempts to reproduce this structure with synthetic alloys of the same composition failed.

A. R. POWELL.

Graphic representation of rock weathering. G. GROSSER (Chem. Erde, 1932, 7, 130—176).—Bulk analyses and analyses of the portions sol. in acid and alkali solutions of fresh and weathered basalt from Oberlausitz, Saxony, are plotted on diagrams.

L. J. SPENCER.

Distribution of tungsten in the Bolivian metal province. F. AHLFELD (Chem. Erde, 1932, 7, 121—129).—Tungsten minerals, mostly wolframite (with ferberite and hübnerite), rarely scheelite and tungstite, are found at many localities in association with the Sn ores. They occur in the inner and outer contact zones of granodiorite and quartz-porphyry of Tertiary age, and belong mainly to a later, lower temp. phase than the Sn ore. Approx. analyses of wolframite and ferberite are given.

L. J. SPENCER.

Dehydration and rehydration of kaolin crystals. H. JUNG (Chem. Erde, 1932, 7, 113—120).—Kaolin can be partly dehydrated without destroying the crystal structure, and H₂O can then be reabsorbed. The completely dehydrated material is amorphous, but at 550° it passes into cryst. α -kaolin, Al₂Si₂O₇. The latter, if not strongly ignited, will absorb H₂O giving one or more hydrated Al silicates, which by further treatment may be reconverted into kaolin.

L. J. SPENCER.

Turquoise. H. JUNG (Chem. Erde, 1932, 7, 77—94).—Turquoise (*d* 2.719) from New Mexico gave, after deducting SiO₂ 2.24, P₂O₅ 34.41, Al₂O₃ 33.42, Fe₂O₃ 4.37, FeO 0.72, CuO 7.70, H₂O 19.35=99.97%, agreeing with the formula (Cu,Fe)O₃(Al,Fe)₂O₃·2P₂O₅·9H₂O. Previous analyses tabulated and plotted show considerable variation, as is to be expected with a mineral that was deposited in a colloidal form.

L. J. SPENCER.

Pyrochlore-romeite group. F. MACHATSCHKI (Chem. Erde, 1932, 7, 56—76).—The several minerals

(pyrochlore, hatchettolite, koppite, pyrrhite, microlite, neotantalite, atopite, schneebergite, romeite, weslienite, mauzeilite, lewisite, and monimolite) of this group have the general formula X₂Z₂(O,OH,F)₇, where X=Na, Ca, Ce, etc., and Z=Nb, Ta, Ti, Sb. They crystallise as small octahedra and have the same type of crystal structure with the edge of the unit cube ranging from 10.27 to 10.41 Å. As chemical varieties of one species they are distinguished as niobpyrochlore (for pyrochlore proper), tantalpyrochlore (microlite), antimonpyrochlore (romeite=atopite), titanantimonpyrochlore (mauzeilite and lewisite), etc.

L. J. SPENCER.

Central American volcanic ashes. E. DEGER (Chem. Erde, 1932, 7, 51—55).—Chemical and mechanical analyses are given of the ash which fell on various dates (24 April—12 June, 1931) after the eruptions of the Izalco volcano in Salvador.

L. J. SPENCER.

Coloured efflorescences and encrustations on Elbe sandstone. E. BLANCK, A. SEIFERT, and F. GIESECKE (Chem. Erde, 1932, 7, 35—50).—Efflorescences of various alums and gypsum have long been known on the Elbe sandstone in northern Bohemia and Saxony. Red and reddish-violet encrustations (or rather surface impregnations) are noted from several localities in Saxony. Analyses are given of the yellow sandstone, the bleached zone, and the coloured encrustation zone. The last contains relatively more P₂O₅ (1.40%) and SO₃ (0.91%), and the colouring is ascribed to Fe and Mn phosphates.

L. J. SPENCER.

Brazilian salt-pans. F. W. FREISE (Chem. Erde, 1932, 7, 24—34).—Salt-pans in the interior of Brazil are with few exceptions confined to the outcrop of Permian rocks. The different types described are those carrying nitrates (K, Ca, Mg), carbonates (Na), sulphates (Na), and NaCl. Analyses of the salts are given.

L. J. SPENCER.

Genesis of the native copper and silver ore deposits in the Lake Superior region. K. NISHIO (Proc. World Eng. Cong., Tokyo, 1931, 37, 499—544).

CHEMICAL ABSTRACTS.

Iron ore from El Tofo, Chile. F. WÜST (Bol. min. Soc. Nac. Min., 1931, 43, 381—385).—The ore, a mixture of magnetite and hæmatite, contained Fe 69.7% and V 0.21%, with little P and S.

CHEMICAL ABSTRACTS.

Liesegang phenomenon applied to Lake Superior iron formations. R. J. HARTMAN and R. M. DICKEY (J. Physical Chem., 1932, 36, 1129—1135).—The peculiar banding of the Fe formations is ascribed to the slow diffusion of sol. Fe^{II} salts through a gel formed by the interaction of basic N compounds, CO₂, or carbonates with Na silicate, giving rise to irregularly-spaced bands of FeCO₃ separated by SiO₂.

F. URBAN (c).

Optical measurements with antimonite. A. CISSARZ (Neues Jahrb. Min., 1931, A, 64, Bl.-Bd., 137—162; Chem. Zentr., 1932, i, 512).

Action of heat on fluorite. L. DOMANGE (Compt. rend., 1932, 194, 1667—1669).—Seven samples of fluorite containing 0—1.12% SiO₂ broke into fragments and emitted violet (or in one case green)

luminescence at 200—300°. They lost 0.013—0.057 wt.-% (H₂O) at 150°, and an additional 0.0066—0.029% (gas) at 400°. Corresponding figures for a sample containing 15% SiO₂ are 300°, 0.54, and 0.51%. The *d* was unaltered, and if any allotropic change occurs, it is completely reversible.

C. A. SILBERRAD.

Transformation of brown coal into bituminous coal. G. STADNIKOV (Brennstoff-Chem., 1932, 13, 101—102).—The Tschereemchov seam (Siberia) consists of layers of coal separated by layers of shale or clay. The upper layers are typical brown coals whilst the lower layers are bituminous coals, an intermediate layer appearing to form a transition stage between the two varieties of coal. The seam is free from folds, faults, or igneous intrusions, so that no theory based on such phenomena can here explain the transformation of the brown coal into the bituminous coal. Theories based on temp. rises due to exothermic reactions also appear to be excluded.

A. B. MANNING.

Climate and parent material in soil formation in S.W. England. A. J. LOW (Nature, 1932, 129, 655).

L. S. THEOBALD.

Soils of the Nile and Gash. VIII. P. VAGLER and F. ALTEN (Z. Pflanz. Düng., 1932, 24 A, 179—242; cf. B., 1932, 476).—Mechanical and chemical data for numerous soils from several areas are recorded. The effectiveness of nutrients in these soils is largely dependent on the rate of H₂O movement through the soil mass. The characteristically high K content of many Egyptian and Sudan soils does not necessarily imply that K fertilisers would not prove beneficial. In these districts K acts not only as a fertiliser but also as an ameliorant by increasing H₂O mobility in the Na-clays. In this respect it is more effective than CaO or gypsum in penetrating to subsoil layers and breaking up the illuvial horizon. For the successful removal of Na salts, thorough surface working prior to leaching is essential.

A. G. POLLARD.

Hinojo meteorite. E. H. DUCLOUX (Anal. soc. cient. Argentina, 1931, 112, 247—252).—The meteorite (1155 g.) contained: SiO₂ 34.33, Al₂O₃ 2.22, FeO 12.29, Fe₂O₃ 16.53, MnO 0.59, NiO 1.39, CoO 0.04, CaO 2.27, MgO 20.04, K₂O 0.19, Na₂O 1.52, P₂O₅ 0.44, Fe 6.61, Ni 0.27, Co 0.01, S 0.54, P 0.08, H₂O and loss on ignition 0.69%. CHEMICAL ABSTRACTS.

Organic Chemistry.

Number of stereoisomeric and non-stereoisomeric paraffin hydrocarbons. C. M. BLAIR and H. R. HENZE (J. Amer. Chem. Soc., 1932, 54, 1538—1545; cf. this vol., 495).—Theoretical. A relationship is established between the no. of stereoisomeric and non-stereoisomeric paraffins and the alkyl groups of which the former may be considered to be composed. Recursion formulæ are advanced for calculating the no. of stereoisomeric and non-stereoisomeric paraffins in each of the structural types (arbitrarily chosen on the basis of their formulæ) from their C content, but their use involves the knowledge of total no. of stereoisomeric and non-stereoisomeric alkyl groups of *N*/2 and all smaller C contents.

C. J. WEST (b).

Thermal decomposition of *n*-butane into primary products. M. NEUHAUS and L. F. MAREK (Ind. Eng. Chem., 1932, 24, 400—402).—The method of Schneider and Fröhlich (this vol., 27) is applied to *n*-C₄H₁₀ pyrolysed at 600° and 650°. The primary products are the following (the no. of mols. for 100 mols. of C₄H₁₀ at each temp. are shown in parentheses); CH₄ and CHMe:CH₂ (48.5, 48.0), C₂H₆ and C₂H₄ (34.5, 37.7), H₂ and butylenes (16.0, 12.3), and C₃H₈ [0, (?) 1.0]. The results for the first two pairs agree with those predicted by Rice (A., 1931, 819). No butadiene, aromatic hydrocarbons, or hydrocarbons of mol. wt. higher than C₄H₁₀ were formed.

A. A. LEVI.

Preparation of $\alpha\beta\gamma\delta$ -tetrabromobutane. R. A. JACOBSON (J. Amer. Chem. Soc., 1932, 54, 1545—1548).— $\beta\gamma$ -Dibromobutane or crotyl chloride (I) is passed over soda-lime at 400—550° and the resulting gaseous products are absorbed in Br; the yields of $\alpha\beta\gamma\delta$ -tetrabromobutane (II) are 13.5—14.5% or 16.4—19.3%. The use of (I) is preferred. The

by-products formed with (II) are: $\alpha\beta$ -, $\alpha\gamma$ -, $\alpha\delta$ -, and $\beta\gamma$ -dibromobutanes, $\alpha\alpha\delta\delta$ -tetrabromobutane, an isomeride of (II), and *trans*- β -bromo- Δ^2 -butene.

C. J. WEST (b).

***p*-Nitrophenylcarbimide as a reagent for alcohols and amino-compounds.** C. W. VAN HOOGLSTRATEN (Rec. trav. chim., 1932, 51, 414—433).—The reaction between PhNCO and H₂O is unimol., the mean val. of *K* at 0° being 0.26. *p*-Nitrophenylcarbimide (I), m. p. 57° [modified prep. from COCl₂ and *p*-nitroaniline; occasional by-product, *p*-nitrocarbonyl chloride, m. p. indef. 120—135°, also prepared from (I) and dry HCl in C₆H₆], reacts violently with H₂O. Attempts to prepare 2:4-dinitrophenylcarbimide failed. When pure, (I) (solid or in solution) has little tendency to polymerise (cf. A., 1897, i, 410), but with a trace of pyridine in dry Et₂O or C₆H₆ forms a *polymeride*, m. p. 340° (block), stable to H₂O at 120° and to EtOH-NH₃, and with EtOH at 120° (not at 100°) forming Et *p*-nitrophenylcarbamate. With KOAc (below 90°) (I) forms (?) *tri-p*-nitrophenylcarbimide, m. p. above 360°. The following *p*-nitrophenylcarbamates were prepared: *n*-octyl, m. p. 111°; *n*-decyl and *n*-dodecyl, m. p. 117°; *n*-stearyl, m. p. 115°; *oleyl*, m. p. 85—91°; CH₂Ph, m. p. 157°; CHPh₂, m. p. 150°; benzoin, m. p. 183°; 5-hydroxy[? hydroxymethyl]furfuraldehyde m. p. 187°; glycol, m. p. 236°; glycerol, m. p. 216°; Ph, m. p. 161°; resorcinol, m. p. 232°. By reaction of (I) with the appropriate base the following substances were prepared: *N*-*p*-nitrophenyl-*N'*-ethyl- (m. p. 158°), *n*-propyl-, m. p. 151°, *n*-butyl-, m. p. 146°, *-dimethyl*-, m. p. 221°, *-diethyl*-, m. p. 162°, and *-di-n-propyl*-, m. p. 130°, *-carbamide*; *N*-*p*-nitrophenylcarbonyl-piperidine, m. p. 164°, and *-pyrrole*, m. p. 280°. Et *p*-nitrophenylallophanate,

m. p. 202° (formed only in presence of pyridine); *p*-nitrophenylhydantoic acid, m. p. 200° (*Et* ester, m. p. 168°); 1-*p*-nitrophenyl-hydantoin, m. p. 244°, -4- and -3-methyl- (m. p. 174° and 161°, respectively), and -4-isobutyl- (m. p. 181°) -hydantoic acid, and -4-dimethylhydantoin, m. p. 176°. The following semicarbazide derivatives, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{NHR}$, were prepared, R being the radical named: *Ph*, m. p. 211—213°; *p*-bromophenyl, m. p. 210°; *o*- (m. p. 225°), *m*- (m. p. 207°), and *p*- (m. p. 212°) -tolyl. Di-(*p*-nitrophenyl)semicarbazide has m. p. 246° and di-(*p*-nitroanilinoformyl)hydrazine, $(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH})_2$, m. p. 276°. The *p*-nitrophenylsemicarbazones of PhCHO and COMe_2 have m. p. 226° and 237°, respectively (from *p*-nitrophenylsemicarbazide, m. p. 186—187°). (I) is well suited for characterisation of alcohols and NH_2 -compounds, but does not react with $\text{CPh}_3 \cdot \text{OH}$. Indole and *Et* dihydrocollidinedicarboxylate do not react with PhNCO . Pyridine catalyses the reaction of (I) with amines, but also causes some polymerisation.

R. S. CAHN.

Stoichiometric additive compounds of alcohols and hydrogen chloride in the liquid state. G. KOHN (Ber., 1932, 65, [B], 589—595).—In confirmation of the hypothesis of the existence of liquid additive compounds of HCl and alcohols, it is shown that saturation of MeOH, EtOH, PrOH, BuOH, and amyl and octyl alcohol with HCl causes absorption of about 8% more HCl than is required to form the 1:1 compound. When amyl alcohol is shaken with aq. HCl the acid is not distributed between the two phases in conformity with the partition coeff., but accumulates in the alcohol with increasing concn. of the aq. phase. In presence of C_6H_6 , ligroin, or paraffin, the ratio HCl: alcohol = 1:1 persists after saturation. The solubility of the adducts differs in certain cases from that of the pure alcohols, the effect being noticeable when only a part of the stoichiometric amount of HCl has been absorbed. Addition of H_2O to the additive compound from EtOH and HCl causes a marked increase in viscosity which attains a max. at the ratio $\text{H}_2\text{O}:\text{HCl} = 1:1$. H_2O can be added to amyl alcohol-HCl until present in 2.4—2.5 times the amount of HCl; further addition causes separation into 2 phases.

H. WREN.

Preparation of absolute isopropanol. L. E. GILSON (J. Amer. Chem. Soc., 1932, 54, 1445).—Abs. Pr^βOH is obtained when the 91% azeotropic mixture is shaken with 10% of its wt. of flake NaOH, separated from the resulting aq. layer, shaken with a further small amount of NaOH, decanted, and distilled. Dil. Pr^βOH is concentrated by shaking with dry NaCl; the resulting upper layer (containing about 87% Pr^βOH and 2—3% NaCl), when distilled, gives practically the 91% mixture. Pr^βOH is recommended as a substitute for EtOH in biochemical work.

L. E. GILSON (b).

Reducing action of the Grignard reagent and the synthesis of *tert*-aliphatic carbinols. A. H. BLATT and J. F. STONE, jun. (J. Amer. Chem. Soc., 1932, 54, 1495—1499; cf. A., 1929, 675).—There is no definite and exact correlation between an increase in the complexity of the alkyl group and

the amount of reduction observed in the reaction between aliphatic ketones and Mg alkyl iodides. The synthesis of *tert*-aliphatic carbinols containing both straight and branched alkyl groups should be effected from branched-chain ketones and Mg *n*-alkyl halides. COPr_2 and MgPrBr give $\text{CPr}_3 \cdot \text{OH}$ (mainly) and $\text{CHPr}_2 \cdot \text{OH}$; COPr_2 and $\text{MgPr}^\beta\text{Br}$ afford $\text{CPr}_2\text{Pr}^\beta \cdot \text{OH}$ (mainly), and small amounts of $\text{CHPr}_2 \cdot \text{OH}$ and a condensation product; COPrPr^β and MgPrBr yield $\text{CPr}_2\text{Pr}^\beta \cdot \text{OH}$ (mainly) and $\text{CHPrPr}^\beta \cdot \text{OH}$; COPrPr^β and $\text{MgPr}^\beta\text{Br}$ furnish $\text{CPrPr}^\beta \cdot \text{OH}$; COPr^β_2 and MgPrBr give $\text{CPrPr}^\beta_2 \cdot \text{OH}$ (mainly) and $\text{CHPr}^\beta_2 \cdot \text{OH}$.

C. J. WEST (b).

Constitution of the mannitol dibenzoate of Einhorn and Hollandt. P. BRIGL and H. GRÜNER (Ber., 1932, 65, [B], 641—645).—Benzoylation of mannitol in presence of H_3BO_3 affords mannitol dibenzoate, m. p. 182°, identical with that prepared by Ohle and others (A., 1930, 191) and by Einhorn and Hollandt. Since it is oxidised by KMnO_4 to benzoylglycollic acid (not dibenzoylmesotartaric acid as assumed by Ohle), it cannot be a $\delta\epsilon$ -derivative. On grounds of probability it is regarded as an α' -compound; this conclusion is strengthened by its inability to react with CPh_3Cl and by the introduction of a Bz group into the 6 position in the analogous benzoylation of glucose and its ethylmercaptal. The following compounds are incidentally described: *Pb glycollate*, $\text{CH}_2 \cdot \text{O} \begin{array}{l} \diagup \\ \text{CO}_2 \end{array} \text{Pb}$; *1-dibenzoyltartaric acid*, m. p. 112—113°, and its *anhydride*, m. p. 182°; *meso-dibenzoyltartaric anhydride*, m. p. 207—208°; *benzoylglycollic acid*, m. p. 112°, and its *anhydride*, m. p. 126°.

H. WREN.

Ring contraction in formation of inner ethers from glycols. Oxidotetradecane from tetradecane- $\alpha\xi$ -diol. A. FRANKE, A. KROUPA, and T. PANZA (Monatsh., 1932, 60, 106—116).—Tetradecane- $\alpha\xi$ -diol, best prepared by reduction of Me dodecymethylenedicarboxylate with Na and amyl alcohol (cf. A., 1926, 499), gives on dehydration by distillation from 50% H_2SO_4 with superheated steam an oxide, $\text{C}_{14}\text{H}_{28}\text{O}$, b. p. 259—262°, in small yield, accompanied by much unsaturated material. Oxidation of the oxide with KMnO_4 in COMe_2 gives decoic acid in good yield, unaccompanied by succinic or oxalic acid. Succinic acid is destructively oxidised by KMnO_4 in COMe_2 , but not by aq. alkaline KMnO_4 ; further, oxidododecane gives *n*-hexoic acid alone with KMnO_4 in COMe_2 , but is known to give oxalic and succinic acids in addition with aq. alkaline KMnO_4 . The $\alpha\xi$ -oxide structure, $\text{C}_9\text{H}_{19} \cdot \text{CH} \begin{array}{l} \diagup \text{CH}_2 \cdot \text{CH}_2 \\ \text{O} \quad \diagdown \end{array} \text{CH}_2$, is therefore assigned to oxidotetradecane.

H. A. PIGGOTT.

Preparation, properties, and uses of glycerol derivatives. IV. Épiethylin, epiphenylin, and phenyl ethers. D. W. STEPHENS (Chem. and Ind., 1932, 375—378).—Improved prep. of glycidyl *Et* ether (epiethylin) (I) [from $\text{CH}_2\text{Cl} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2\text{Cl}$ by NaOH in EtOH to give $\text{CH}_2\text{Cl} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OEt}$ (67% yield), which, by further action of NaOH at 100°, the mixture being kept just acid to phenolphthalein, affords (1) a const. b. p. mixture of (I) and H_2O ,

b. p. 90—124° (25%), (2) (I), b. p. 124—126° (49%), and (3) b. p. >126° (26%), whence by salting out and fractionation a 78% yield of (I) is obtained], Ph glycidyl ether (epiphenylin) (II) [by addition of NaOH to PhOH and CH₂Cl·CH(OH)·CH₂Cl at 70—80°, the reaction mixture being kept just acid to phenolphthalein, heating to 100°, and fractionation of the upper layer which gives a 65% yield of (II), b. p. 115—116°/3—4 mm., OPh·CH₂·CH(OH)·CH₂·OPh, m. p. 80—81° (III), being obtained as a by-product], and OHCH₂·CH(OH)·CH₂·OPh, softens at 50°, becoming liquid at 68° [by a similar method from OH·CH₂·CH(OH)·CH₂Cl, 59% yield], are described. (III) is similarly prepared from PhOH and CH₂Cl·CH(OH)·CH₂Cl at 120° (70—75% yield). F.-p. diagrams for (II)—camphor [eutectic, 31.0°, 61.2 mol.-% of (II)], (III)—camphor [eutectic, 48.0°, 38.4 mol.-% of (III)], and (II)—(III) [eutectic 41.4°, 78.6 mol.-% of (II)], are plotted. (I) and (II) readily afford amino-ethers by the action of bases: NHR₂ + $\begin{matrix} \text{O} \\ \text{CH}_2 \end{matrix} \text{CH} \cdot \text{CH}_2 \cdot \text{OR}' \rightarrow \text{NR}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OR}'$.

J. W. BAKER.

Esters of glycerol with amino-acids, and mixed esters with amino- and fatty acids. II. L. HASKELBERG (Bull. Soc. chim., 1932, [iv], 51, 212—230; cf. this vol., 364).—Glycerol heated with pyruvic acid at 105—110° for 3—4 hr. gives 2H₂O, a solid (I), (?) $\alpha\gamma$ -ethylideneglycerol- α' -carboxy- β -lactone, m. p. 83.5°, b. p. 100—102°/6 mm. (cf. A., 1930, 193), and a liquid *isomeride* (II), (?) $\alpha\beta$ -ethylideneglycerol- α' -carboxy- γ -lactone, b. p. 118—119°/10 mm., converted by warm H₂O into (I). The *isomeride*, m. p. 62°, obtained by Brigl (*loc cit.*) was not observed. (I) gives a *phenylhydrazone*, m. p. 156° (*Bz*₂ derivative, m. p. 188°), whilst with Ba(OH)₂ it gives the *Ba* salt of the corresponding acetal acid. (II) gives an *oxime*, m. p. 119° [*Bz*₃ derivative (III), m. p. 111—112°], and a *phenylhydrazone*, m. p. 114° (*Bz*₂ derivative, m. p. 152°), hydrolysed to pyruvic acid phenylhydrazone. Action of 1% NH₃ in EtOH gives the *amide*, m. p. 81°, of the corresponding acid (*Ba* salt). *iso*Propylideneglycerol with bromopropionyl bromide in presence of pyridine gives *isopropylideneglyceryl* α -*bromopropionate*, b. p. 138°/19 mm., 120°/5 mm., converted by NaNO₂ into the *oximino*-derivative, m. p. 43° [*Bz* derivative, m. p. 107° (softens 104°)], hydrolysed to *glyceryl* α -*oximino*-*propionate*, m. p. 118.5° [*Bz*₃ derivative, m. p. 78.5—79°, not identical with (III)].

A. A. LEVI.

Thionitrites. III. Thermal dissociation of alkyl thionitrites. H. RHEINOLDT and F. MOTT (J. pr. Chem., 1932, [ii], 133, 328—330; cf. A., 1931, 820).—*tert.*-Bu thionitrite (I) in CO₂ or air at 95—98°, or in boiling hexahydrotoluene gives NO and *tert.*-Bu disulphide, b. p. 74°/12 mm.; slow, spontaneous decomp. in air gives an oil and a little cryst. substance. (I) is stable to O₂ at 0°.

R. S. CAHN.

Preparation and properties of a double series of aliphatic mercaptans. L. M. ELLIS, jun., and E. E. REID (J. Amer. Chem. Soc., 1932, 54, 1674—1687).—*n.* and α -*sec.*-Mercaptans from Me to nonyl and various intermediate alcohols and bromides are

prepared. Curves illustrating certain relationships between the mercaptans and alcohols are given. Vals. (new and lit.) of the b. p./760 mm., d_4^{20} , d_4^{25} , expansion per °C., n_D^{20} , and MR_D (found and calc.) for the alcohols from amyl to nonyl (both *n.* and *sec.*-isomerides), for the bromides, and for the mercaptans are given. C. J. WEST (b).

Action of some mercaptans in hydrocarbon solution on copper and copper sulphide. K. H. SLAGLE and E. E. REID (Ind. Eng. Chem., 1932, 24, 448—451).—The action of Cu compounds in removing mercaptans from hydrocarbon solutions is due to the formation of Cu mercaptides, and disulphides (cf. A., 1931, 1033). Measurements are recorded with CuS on Me to *n.*-nonyl, Pr ^{β} , Bu ^{β} , and β -amyl mercaptans in C₆H₆, *n.*-heptane, and cyclohexane. *sec.*-Mercaptans higher than C₄ in C₆H₆ form sol. coloured Cu mercaptides. Repeated treatment with small amounts of CuS is more efficient than a single treatment. The effect of varying concn. was measured with CuS on Bu ^{α} SH in C₆H₆. HgS (black), PbS, Sb₂S₃ (black), CdS, and C are less effective than CuS, whilst other substances have little or no action. Sulphides and disulphides are not attacked. A. A. LEVI.

Addition of alkali alkoxide to esters. V. Ester-alkoxide compounds and acetoacetic condensation. F. ADICKES (Ber., 1932, 65, [B], 522—525; cf. A., 1931, 196).—A criticism of Scheibler's theories. H. WREN.

Addition of alkali enolates to esters. VI. F. ADICKES, W. BRUNNERT, O. LÜCKER, and G. SCHÄFER.—See this vol., 614.

Catalytic hydrogenation of esters to alcohols. II. K. FOLKERS and H. ADKINS (J. Amer. Chem. Soc., 1932, 54, 1145—1154; cf. A., 1931, 598).—Various alkyl mono- and di-carboxylates are hydrogenated to the corresponding alcohols or glycols in 90—98% yields. The rate of hydrogenation is retarded by free acid or MeOH and is considerably modified by the nature of the alkyl group. Thus, cyclohexyl hexoate is reduced much more rapidly than the Et ester, whilst the latter is hydrogenated several times faster than the Me ester. The presence of a Ph, CO₂Et, or CH₂·OH group in the vicinity of a CO₂Et or CH₂·OH group (except with Et lactate) facilitates fission of the C·O linking; the CO₂Et (or CH₂·OH) and CH·OH groups are thus reduced to Me and CH₂, respectively. This reaction occurs almost exclusively when Ph is adjacent to CO₂Et, or when CO₂Et or CH₂·OH is α - to the ester group. Incorporation of Mg or Ca into the catalyst minimises the conversion of the α -Ph esters into the hydrocarbons. *N.*-Hexoylpiperidine is hydrogenated to *N.*-hexylpiperidine. The N·C linking in *N.*-C·C·CO₂Et undergoes fission under the conditions used for hydrogenation of the ester. With Et nipecotate, fission occurs (over Ni) at 165°, and 3-methyl-2-piperidone (or its reduction products) results. The rate of hydrogenation of Et laurate at pressures of 100, 200, and 300 atm. shows a 28-fold increase over this range. The hydrogenation of esters under the conditions used occurs at about 200° upward.

C. J. WEST (b).

Action of ammonia and amines on esters of unsaturated acids. I. Action of ammonia, methylamine, and diethylamine on ethyl crotonate. K. MORSCH (Monatsh., 1932, 60, 50—68).—Interaction of NH_3 and Et crotonate in abs. EtOH at room temp. gives an equilibrium (?) mixture of Et β -aminobutyrate and Et₂ $\beta\beta'$ -iminodibutyrate, accompanied, if the reaction is prolonged, by small amounts of β -aminobutyramide, m. p. 73—74.5°, but traces only of crotonamide. Addition to the double linking is therefore much more rapid than amidation. Similar results are obtained with liquid NH_3 at room temp., but at 100—155° aldehyde-ammonia and NH_4 oxamate are produced, presumably by hydrolytic fission at the double linking. Reaction is considerably more rapid with NH_2Me in abs. EtOH at room temp. or in absence of a solvent at 65°; Et β -methylaminobutyrate (I) is first formed (in 89% yield with 1.1 equiv. NH_2Me) and is converted by further action of NH_2Me into β -methylaminobutyramide. Neither crotonmethylamide nor an imino-ester was formed, and the latter could not be prepared by interaction of Et crotonate and (I). NHEt_2 alone or in abs. EtOH at room temp. reacts very slowly to give Et β -diethylaminobutyrate as main product, but at 200° in absence of a solvent crotondiethylamide, b. p. 100—102°/13 mm., and unidentified basic products are formed. The above Et alkylaminobutyrate are readily hydrolysed by warm H_2O to β -methylamino-, m. p. 141—142° (+ H_2O , m. p. 86—87°), and β -diethylamino-, m. p. 72.5—74.5°, butyric acids. H. A. PIGGOTT.

New example of the allylic isomerisation. A. KIRRMANN and R. RAMBAUD (Compt. rend., 1932, 194, 1168—1170).— Ac_2O converts Et α -hydroxy- Δ^{β} -butenoate into the corresponding Ac derivative, $\text{CH}_2\text{:CH:CH(OAc):CO}_2\text{Et}$ (I), b. p. 89°/15 mm. (hydrolysed to the original acid), but PBr_3 gives Et γ -bromo- Δ^{α} -butenoate, converted by NaOAc into an Ac derivative, b. p. 119—120°/15 mm., isomeric with (I) and hydrolysed to an isomeric acid of the original acid.

J. W. BAKER.

Conjugated double linkings. XXIV. Synthesis of *cis-trans*-isomeric methylated polyene-carboxylic acids. Synthesis and configuration of dehydrogeranic acid. R. KUHN and M. HOFFER (Ber., 1932, 65, [B], 651—660).—The synthesis of a series of *cis-trans*-isomeric methylated polyene-carboxylic acids is described. In view of the uncertainty of the configuration of the isomerides, it is recommended to apply the term "acid I" (probably *trans* with reference to the double linking vicinal to the CO_2H group) to the isomeride of higher m. p. and "acid II" (probably *cis*) to that of lower m. p. The requisite OH-esters are obtained from the ketone, $\text{CH}_2\text{Br:CO}_2\text{Me}$, and Zn in C_6H_6 , whereby aliphatic ketones require 15 min. ebullition and aromatic ketones 3 hr. Ethylideneacetone affords *Me* β -hydroxy- β -methyl- Δ^{γ} -hexenoate, b. p. 82—85°/12 mm., transformed by P_2O_5 in boiling C_6H_6 into *Me* β -methylsorbate, b. p. 80—84°/12 mm., hydrolysed by KOH-EtOH to β -methylsorbic acid I, m. p. 119—120°, and by aq. Ba(OH)_2 to β -methylsorbic acid II, m. p. 98—99° (in addition to

much ethylideneacetone and AcOH). Crotylideneacetone gives *Me* β -hydroxy- β -methyl- $\Delta^{\gamma\epsilon}$ -octadienoate, b. p. 90—105°/3 mm., dehydrated to *Me* β -methyl-octatrienoate, b. p. 117—125°/11 mm., m. p. 33°, whence by KOH-EtOH , β -methyl- $\Delta^{\gamma\epsilon}$ -octatrienoic acid I, m. p. 160—161° (corr.), and impure β -methyl- $\Delta^{\gamma\epsilon}$ -octatrienoic acid II, m. p. 105—110° after softening at 97°; a similar mixture is obtained by means of Ba(OH)_2 . β -Methylcrotonaldehyde, COMe_2 , and aq. NaOH afford ζ -methyl- $\Delta^{\gamma\epsilon}$ -heptadien- β -one, b. p. 86—87°/15 mm. [oxime, m. p. 108—109° (corr.)], transformed into the corresponding OH-ester, which with aq. Ba(OH)_2 yields $\beta\zeta$ -dimethyl- $\Delta^{\gamma\epsilon}$ -octatrienoic acid II, m. p. 137° (corr.), and is converted by P_2O_5 in C_6H_6 into *Me* dehydrogeranic acid, b. p. 127—135°/12 mm., which gives $\beta\zeta$ -dimethyl- $\Delta^{\gamma\epsilon}$ -octatrienoic acid I, m. p. 185—186° (corr.), identical with natural dehydrogeranic acid. Styryl Me ketone affords *Me* β -styrylcrotonate, b. p. 170—172°/12 mm., hydrolysed by KOH-EtOH to δ -phenyl- β -methyl- $\Delta^{\gamma\epsilon}$ -pentadienoic acid II, m. p. 123.5—124.5°, isomerised by I in C_6H_6 in sunlight to δ -phenyl- β -methyl- $\Delta^{\gamma\epsilon}$ -pentadienoic acid I, m. p. 160°. Cinnamylideneacetone slowly affords *Me* β -styrylacrylcrotonate, b. p. 160—180°/0.3 mm., hydrolysed by KOH-EtOH to a mixture of ζ -phenyl- β -methyl- $\Delta^{\gamma\epsilon}$ -heptatrienoic acids, m. p. 202—203° and m. p. 167—169° (corr.), separable into its components by crystallisation from 96% EtOH or, more conveniently, by fractional digestion of the Ba salts with boiling H_2O .

H. WREN.

Synthesis of dehydrogeranic acid and other compounds from β -methyl- Δ^{α} -butenal. F. G. FISCHER and K. LÖWENBERG (Annalen, 1932, 494, 263—284).— β -Methyl- Δ^{α} -butenal (I) (improved prep. given; cf. A., 1931, 335) with aq. Ba(OH)_2 in Et_2O gives (after repeated fractional distillation) impure dehydrocitril (II), b. p. 81—84°/0.3 mm. [semicarbazone, m. p. 223° (decomp.)], and impure β -methyl- $\Delta^{\beta\gamma}$ -heptadien- ζ -one (III) [the pure ketone, b. p. 83—83.5°/9 mm., is prepared from (I) and COMe_2 in EtOH-NaOEt] [semicarbazone, m. p. 192° (decomp.)]; (III) is formed by hydrolytic fission of (II) or the intermediate aldol. (I) is converted by NaNH_2 in dry Et_2O and N_2 into 2-formyl-1:1:5-trimethyl- $\Delta^{2:4}$ -cyclohexadiene (IV) (50% yield), b. p. 85—86°/9 mm. (semicarbazone, m. p. 213°), oxidised by O_3 in EtCl at -30° to $\alpha\alpha$ -dimethyl-lævulic acid (1 mol.) and HCO_2H (2 mols.), and reduced to 2:2:4-trimethylhexahydrobenzaldehyde (semicarbazone, m. p. 222—223°), which is readily autoxidised to 2:2:4-trimethylhexahydrobenzoic acid, m. p. 93°. (IV), COMe_2 , and NaNH_2 in N_2 give 1:1:5-trimethyl-2- γ -keto- Δ^{α} -butenyl- $\Delta^{2:4}$ -cyclohexadiene, b. p. 102—105°/0.8 mm. [semicarbazone, m. p. 190—191° (decomp.)]. Citral is converted by NaNH_2 in Et_2O into a compound, $\text{C}_{20}\text{H}_{30}\text{O}$ (probably 2-formyl-1-methyl-1:5-di- Δ^{γ} -isohexenyl- $\Delta^{2:4}$ -cyclohexadiene), b. p. 203—205°/9 mm., whilst crotonaldehydesimilarly gives resinous material.

(I), $\text{CH}_2\text{Br:CO}_2\text{Et}$, and Zn in C_6H_6 give (after distillation of the intermediate with Zn dust) Et δ -methylsorbate, b. p. 82—83°/9 mm., hydrolysed to δ -methylsorbic acids II, b. p. 123—124°/9 mm., m. p. 17° (main product), and I, m. p. 109—110°, both of which are reduced catalytically to isoheptoic acid.

Hydrolysis of the twice-distilled ester from (III), $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$, and Zn affords $\beta\zeta$ -dimethyl- $\Delta^{\alpha\gamma\epsilon}$ -octatrienoic acid (V), m. p. 187—188° (decomp.), identical with the dehydrogeranic acid of Cahn *et al.* (this vol., 144); hydrolysis of the once-distilled ester gives a little (V) and (mainly) an oily acid, which when heated at 50—95° loses CO_2 forming the readily polymerised $\beta\zeta$ -dimethyl- $\Delta^{\alpha\gamma\epsilon}$ -heptatriene, b. p. 53—54°/10 mm., m. p. —23° to —22°. H. BURTON.

Hydrogenation of arachis oil. H. I. WATERMAN and (FRL.) M. ZAAVER (Rec. trav. chim., 1932, 51, 401—406).—Selective hydrogenation (Ni) of linoleic acid and its glycerides in arachis oil occurs when Normann's but not when Wilbuschewitsch's apparatus is used. Linoleic acid is considered to occur in large quantities in natural edible fats, but to be oxidised when the fats are kept. R. S. CAHN.

Polymerisation and ring formation. XI. Use of molecular evaporation as a means for propagating chemical reactions. XII. Linear superpolyesters. XIII. Polyamides and mixed polyester-polyamides. XIV. Linear superpolyanhydride and cyclic dimeric anhydride from sebacic acid. XV. Artificial fibres from synthetic linear condensation superpolymerides. W. H. CAROTHERS and J. W. HILL. XVI. A polyalcohol from dimagnesium decamethylene bromide. W. H. CAROTHERS and J. E. KIRBY (J. Amer. Chem. Soc., 1932, 54, 1557—1559, 1559—1566, 1566—1569, 1569—1579, 1579—1587, 1588—1590).—XI. The use of mol. evaporation in reversible reactions involving the simultaneous formation of volatile and non-volatile products is advantageous. A new form of mol. still is described.

XII. The term superpolymeride is applied to linear polymerides of mol. wt. above 10,000. The previously described (A., 1930, 1272 and previous abstracts) linear polyesters derived from dibasic acids and glycols or from higher ω -OH-acids, when heated in a mol. still or in an inert gas, undergo self-reaction forming polyesters of much higher mol. wt. The new superpolyesters (ω -polyesters) are tough opaque solids; they show sharp X-ray powder diffraction patterns, become transparent at definite temp., and dissolve in CHCl_3 giving highly viscous solutions. The ω -trimethylene ester, m. p. 75—76°, M 3300, of hexadecamethylene- $\alpha\pi$ -dicarboxylic acid is prepared when the acid and 10% excess of the glycol are heated first at 180—200° for 3 hr. and then at 200°/ <1 mm. for 6 hr. When this ester is heated at 200° (bath)/ $<10^{-3}$ mm. for 7 days in a mol. still a (non-distillable) product, M 12,000, results; the small amount of distillate contains (probably) unimol. trimethylene hexadecamethylene-dicarboxylate, m. p. 124—125°. ω -Polyethylene succinate, a tough, somewhat elastic mass, softens at 95° to a very viscous and somewhat rubbery mass; fibres of this are short and rather brittle. The ω -polyester from λ -hydroxydecoic acid is a translucent tough, flexible mass. The ω -ester from ξ -hydroxy-pentadecanoic acid becomes transparent at 95°, and can be drawn into thin fibres and cold drawn.

XIII. The polyamide derived from ϵ -aminohexanoic acid (A., 1931, 205), when heated in the mol. still, undergoes a considerable change in physical properties,

indicating an increase in mol. wt. When ϵ -aminohexanoic (1—5 mols.) and 1 mol. of hexadecamethylene- $\alpha\pi$ -dicarboxylic acids are heated with $(\text{CH}_2)_3(\text{OH})_2$ (1 mol. + 5% excess), mixed polyester-polyamides are obtained (the m. p. increases with the amount of NH_2 -acid). The properties of these substances are between those of the polyesters and the polyamides; like the superpolyesters they can be drawn out into strong, pliable, transparent fibres.

XIV. Sebacic α -anhydride, M about 5000, from the acid and AcCl or Ac_2O , is a linear polymeride. Smooth depolymerisation of this anhydride cannot be effected by ordinary vac. distillation, but when heated in the mol. still a (more complex) ω -anhydride (I), and the volatile β -anhydride (II), m. p. 68°, are obtained. (I) is very tough and can be drawn into exceedingly strong, pliable, lustrous, highly-oriented fibres. (II) is a cyclic (22-membered ring) dimeride. When heated above its m. p., (II) polymerises to a γ -anhydride, which resembles the α -anhydride. The behaviour of these anhydrides towards NH_2Ph is described and discussed.

XV. The linear condensation ω -polyesters, polyanhydrides, and mixed polyester-polyamides, described above, are easily drawn out into very strong, pliable, highly-oriented fibres which closely simulate natural silk and cellulose fibres. These materials also resemble cellulose and silk in the essential details of their mol. structure. If no stress is used in the prep. of the filaments they closely resemble the massive ester from which they are produced; if sufficient tension is applied the filaments are transparent and have a very high lustre. The tensile strength of rather thick fibres of the ω -trimethylene hexadecamethylene- $\alpha\pi$ -dicarboxylate, prepared by pulling filaments from the molten ester and subsequently orienting them by cold drawing, is approx. 16—24 kg. per sq. mm.; the dry (or wet) tenacity is about 1.1 g. per denier. The fibres are more elastic than those of any known artificial silk. The fibres from the anhydrides have a very high degree of strength, pliability, and lustre, but they gradually disintegrate on keeping, owing to hydrolytic degradation.

XVI. $(\text{CH}_2)_{10}(\text{MgBr})_2$ and HCO_2Me give an alcohol $[(\text{CH}_2)_{10}\text{CH}\cdot\text{OH}]_5$, m. p. 120—121°; various derivatives (e.g., Ac) are obtained as oils or tars. When heated in the mol. still, a product of the same composition but much higher mol. wt. results.

C. J. WEST (b).

Structure of the glutaconic acids and esters. III. α -Carbethoxyglutaconic esters. B. S. GIDVANI, G. A. R. KON, and C. R. WRIGHT (J.C.S., 1932, 1027—1040; cf., A. 1931, 608).—Carbethoxyglutaconic esters and NaOEt afford Na derivatives, partly hydrolysed by H_2O to an equilibrium mixture of $\alpha\beta$ - and $\beta\gamma$ -forms. The $\beta\gamma$ -ester is liberated from the remaining alkaline solution by CO_2 ; also by BzOH from the Na or K derivatives in a neutral solvent. All the esters studied alkylate in the α -position. The Na derivative of Et isoconitate ($\beta\gamma$ -ester) reacts with MeI in EtOH to give an α -alkyl compound, which on ozonolysis affords Et glyoxylate and Et α -formylmethylmalonate (phenylhydrazone, m. p. 128°), and with NaOEt during 1 hr. affords Et α -methylglutaconate. Et β -chloro-crotonate and -iso-

crotonate with Et sodiomalonate afford distinct tricarboxylic esters, hydrolysed by 5% KOH to acids, m. p. 149° (from *trans*-ester) and m. p. 115—116° (from *cis*-ester), respectively. The K derivative of Et α -carbethoxy- β -methylglutaconate ($\alpha\beta$ - and $\beta\gamma$ -forms) affords with BzOH the pure $\beta\gamma$ -ester and with MeI, an α -Me compound, ozonised to Et glyoxylate and Et acetylmethylmalonate (*pyrazolone*, m. p. 176°). The methylated product and NaOEt afford Et $\alpha\beta$ -dimethylglutaconate, hydrolysed to the *cis*- $\alpha\beta$ -acid. Et phenylpropionate and Et sodiomalonate afford a yellow Na compound (Na in γ -position) which is not methylated in a neutral solvent. HCl liberates a liquid ester ($\alpha\beta$ - and $\beta\gamma$ -forms) affording a colourless Na derivative (Na in α -position) which suffers α -alkylation and affords the $\beta\gamma$ -isomeride with BzOH. The reaction product of Et phenylpropionate and Et sodiomethylmalonate with HCl (but not with BzOH) affords the $\beta\gamma$ -ester. γ -Me and -Et carbethoxyglutaconates react normally; the CH_2Ph ester, in the equilibrium state contains some $(\text{CO}_2\text{Et})_2\text{CH}\cdot\text{CH}_2\cdot\text{C}(\cdot\text{CHPh})\cdot\text{CO}_2\text{Et}$, the K derivative of which affords with BzOH no $\alpha\beta$ -ester, although some benzylidene ester is formed. Reaction of the γ -Me ester with Al-Hg in Et_2O affords *Et* α -carbethoxy- γ -methylglutarate, b. p. 159—161°/14 mm. Interaction of Et α -carbethoxy- γ -methyl- α -ethylglutaconate and Et α -carbethoxy- α -methyl- γ -ethylglutaconate with NaOEt affords dibasic esters which immediately suffer interconversion and afford only mixtures of isomerides. J. L. D'SILVA.

Alkylaconitic acids. R. D. DESAI (J.C.S., 1932, 1088—1093).—Alkylation of Et aconitate affords a viscous product, and poor yields of the aconitic esters are obtained from $\text{CH}_2(\text{CO}_2\text{Et})_2$ or $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ with Et chlorofumarate and up to 3 mols. NaOEt. Et oxalacetate and Et bromopropionate with Zn in C_6H_6 afford *Et* α -methylcitrate, b. p. 195°/15 mm., in small yield and NPhEt_2 with Et α -bromotricarballylate affords mainly the lactone of Et_2H α -hydroxytricarballylate and some aconitic acid. Ozonolysis shows that Et α -cyanoaconitate (J.C.S., 1906, 89, 631) is a mixture of the $\alpha\beta$ - and $\beta\gamma$ -forms (I). Et oxalocyanacetate, one product of ozonolysis, affords with semicarbazide acetate 3-carbethoxy-1-carbamyl-4-cyanopyrazolone, m. p. 237° (decomp.). The K derivative of (I) affords with BzOH the $\alpha\beta$ -ester with some $\beta\gamma$ -ester (cf. A., 1930, 773). Methylation of the K salt affords Et α -cyano- Δ^a -butene- $\alpha\beta\gamma$ -tricarboxylate, the isomeric " $\beta\gamma$ -ester" (J.C.S., 1906, 89, 631) containing some $\alpha\beta$ -ester. Further methylation of the $\alpha\beta$ - or $\beta\gamma$ -form affords the dimethylated ester. Hydration of α -methylaconitic anhydride affords the *cis*-acid, m. p. 105°, converted into the *trans*-acid by HCl or heat. With AcCl in CHCl_3 , α -methylaconitic acid affords the *anhydro*-acid(?), m. p. 110° (decomp. 140°). J. L. D'SILVA.

d-Talonic acid and γ -talonolactone. L. H. CRETCHER and A. G. RENFREW (J. Amer. Chem. Soc., 1932, 54, 1590—1594).—Freshly prepared solutions of *d*-talonic acid, $[\alpha]_D^{25} +18.24$ — 19.65° (cf. A., 1927, 340), give no evidence of γ -lactone when titrated with 0.1N-NaOH; nearly 4% is found after 1 hr. The % of γ -lactone calc. from titration vals. are definitely

higher than those calc. polarimetrically during the first 24 hr. The shape of the mutarotation curve for solutions of talonic acid indicates the formation of a dextrorotatory δ -talonolactone, in addition to the laevorotatory γ -lactone. γ -Talonolactone has m. p. 132—134°, $[\alpha]_D^{25} -34.65^\circ \rightarrow -28.4^\circ$ (5 days) in H_2O . C. J. WEST (b).

Manufacture of calcium gluconate by electrolytic oxidation of glucose. H. S. ISBELL, (Miss) H. L. FRUSH, and F. J. BATES (Ind. Eng. Chem., 1932, 24, 375—378).—The process already described (A., 1931, 1038) is made continuous for the prep. of Ca gluconate (yield 85%). Directions are given for recovery of the bromide. Basic Ca gluconate is $\text{Ca}(\text{C}_6\text{H}_{11}\text{O}_7)_2 \cdot 2\text{CaO}$. A. A. LEVI.

Micro-determination of uronic anhydride groups in pectic substances. H. W. BUSTON (Analyst, 1932, 57, 220—223).—In a modified micro-Zeisel apparatus, 6—10 mg. of the substance are refluxed with 4 c.c. of 13% HCl (90% saturated with NaCl) for 60—70 min. Any HCl is removed by Ag_2SO_4 and CO_2 is absorbed from a sintered glass plate in 0.02N-Ba(OH) $_2$. An aliquot portion of the $\text{Ba}(\text{OH})_2$ solution is titrated with 0.01N- $\text{H}_2\text{C}_2\text{O}_4$. T. MCLACHLAN.

Behaviour of methylglyoxal in weak alkaline solution. Y. ARAI (J. Biochem. Japan, 1932, 15, 151—161).—Methylglyoxal is rapidly transformed quantitatively into lactic acid when treated with alkali at reactions exceeding p_H 13.0, whilst at smaller degrees of alkalinity AcOH , HCO_2H , and unknown reducing substances are formed in addition to lactic acid, the proportions of the products depending on the degree of alkalinity and on the temp. KCN accelerates the disappearance of methylglyoxal and increases the yield of reducing substances. F. O. HOWITT.

Nitroso-compounds. I. Preparation and reduction of nitrosoketones. J. G. ASTON, D. F. MENARD, and M. G. MAYBERRY (J. Amer. Chem. Soc., 1932, 54, 1530—1538).—Ketones of the type $\text{CHMe}_2\cdot\text{CO}\cdot\text{CH}_2\text{R}$, treated with an equiv. quantity of Et nitrite in HCl at about 50°, afford some of the bimol. compounds $(\text{NO}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{CH}_2\text{R})_2$. Thus COMePr^B gives 24% of bimol. *Me nitrosoisopropyl ketone* (I), m. p. 101.5—102° (decomp.); COEtPr^B affords 6.8% of bimol. *Et nitrosoisopropyl ketone*, m. p. 119—120°, and 27% of *Pr α -oximinoethyl ketone*, m. p. 92—93°. Reduction of (I) with SnCl_2 and HCl gives 62% of β -azoxy- β -methylbutan- γ -one, m. p. 60—61°, reduced further to COMePr^B and N_2H_4 . Reduction of bimol. β -nitroso- β -methylpentan- δ -one with SnCl_2 and HCl or Na-Hg and H_2O gives neither the corresponding amine nor hydrazine. There is no evidence that, as a rule, the NO group in aliphatic compounds is reduced to NH_2 or $\text{NH}\cdot\text{OH}$ except in small yields. C. J. WEST (b).

Constitution of certain carbohydrates. W. N. HAWORTH (Ber., 1932, 65, [4], 43—65).—A lecture. H. WREN.

Oxidation of the α - and β -forms of the sugars. H. S. ISBELL (J. Amer. Chem. Soc., 1932, 54, 1692—1693).—There are marked differences in the rates of oxidation of various sugars and of different forms of a given sugar with $\text{Br}\cdot\text{H}_2\text{O}$. β -Lactose is oxidised to

about 95% in 3 min., whilst α -lactose undergoes about 50% oxidation. This affords a method of determining the approx. amounts of the α - and β -isomerides in solution.

C. J. WEST (b).

Behaviour of phenolphthalein and methyl-orange in the oxidation of sugars by alkaline iodine. (Miss) C. A. MALLIN (Analyst, 1932, 57, 244—245).—With I in the presence of alkali, phenolphthalein forms tetraiodophenolphthalein and EtOH gives rise to CHI₃; together these may cause an error of 2% and account for the results of Slater and Acree (cf. A., 1930, 1165). Aq. methyl-orange is unaffected by alkaline I.

T. MCLACHLAN.

Synthesis of 2:3:6-trimethylglucose. J. C. IRVINE and J. K. RUTHERFORD (J. Amer. Chem. Soc., 1932, 54, 1491—1495).—2:3-Dimethylmethylglucoside and 30% HNO₃ in CHCl₃ give 89% of its 4:6-dinitrate, converted by NaI in COMe₂ at 100° into 6-iodo-2:3-dimethylmethylglucoside 4-nitrate. Treatment of this with AgOAc, hydrolysis (alkaline) of the product formed, and subsequent methylation gives 2:3:6-trimethylmethylglucoside 4-nitrate, reduced by Fe and AcOH to a trimethylmethylglucoside, b. p. 130—140°/0.2 mm., which is hydrolysed to 2:3:6-trimethylglucose, m. p. 114°.

C. J. WEST (b).

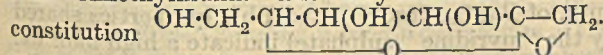
Determination of fructose and sucrose. J. FIEBE (Z. Unters. Lebensm., 1932, 63, 288—291).—The solution is heated on a water-bath for 30 min. with 10 c.c. of 5N-HCl, diluted to 50 c.c., and 5 c.c. are pptd. with 5 c.c. of 32% HCl and 0.625% phloroglucinol (cf. B., 1929, 146, 375, 955). Arabinose gave a bluish-green colour, and glucose, maltose, lactose, and wheat starch (1%) yellow colours, but no ppt.; 10 c.c. of 1% sucrose yielded 12.36 mg., and 5 c.c. of 1% fructose 11.71 mg. of hydroxymethylfurfuraldehyde, these results being reproducible within 0.5% if more than 11 mg. are weighed. Under these conditions 50 mg. of sucrose give the same wt. of ppt. as 26.3 mg. of fructose, but for more conc. solutions relatively higher wts. of ppt. are obtained.

J. GRANT.

Structure of α -fructose penta-acetate and α -fructose chloro[tetra]acetate. E. PACSU and F. V. RICH (J. Amer. Chem. Soc., 1932, 54, 1697—1698).—It is suggested that α -fructose chlorotetra-acetate is a derivative of the open-chain fructose with a Cl atom at C₆.

C. J. WEST (b).

Constitution of the anhydrofructose of Irvine and Stevenson. H. H. SCHLUBACH and H. ELSNER (Ber., 1932, 65, [B], 519—522; cf. A., 1929, 1046).—Treatment of anhydrofructose triacetate, m. p. 122°, [α]_D²⁰ -1° in CHCl₃, obtained from inulin by the method of Irvine and Stevenson, with NaOH and Me₂SO₄ followed by Ag₂O and MeI affords a product which, after depolymerisation with EtOH-H₂C₂O₄ and hydrolysis, yields 3:4:6-trimethylfructofuranose (phenylosazones, m. p. 78—80° and 123—125°, respectively), identical with that obtained by Haworth and Learner from trimethylinulin. The anhydrofructose has the constitution



The question of its identity with lavan is left open. Irvine and Stevenson's views concerning the heterogeneity of inulin are untenable.

H. WREN.

Heptamethylsucrose: a correction. J. C. IRVINE and E. T. STILLER (J. Amer. Chem. Soc., 1932, 54, 1486—1491).—The "heptamethylsucrose" described by Haworth (J.C.S., 1923, 123, 301) is a complex mixture containing 30% of octamethylsucrose. Hydrolysis of the mixture gives tetramethyl- γ -fructose (45%), tetramethylglucose (15%), trimethyl- γ -fructoses (8%), 17% of four isomeric forms of trimethylglucose, and 14% of a mixture of 2:3-dimethylglucose, one other isomeride, and monomethylglucoses. Evidence is obtained showing the order in which Me groups enter the sucrose mol.; so far as the glucose component is concerned, this is similar to that in starch. Methylation of sucrose may be accompanied to some extent by alteration in the position of the O ring in the glucose component.

C. J. WEST (b).

9:9-Diacetamido-compound of alizarin-glucoside. A. MÜLLER (Ber., 1932, 65, [B], 672—679; cf. A., 1931, 940).—1-Acetoxy-2-acetoglucosoxy-anthraquinone-9-imine (I) (improved prep.) is transformed by 15% NH₃-MeOH into 9:9-diacetamido-1-hydroxy-2-glucosoxyanthraquinone (II), m. p. 154—155° after becoming red at 120°, [α]_D²⁰ -59.26° in H₂O, obtained similarly from the *N*-Ac derivative of (I). It is stable towards alkali, but hydrolysed by 5% HCl to alizarin-glucoside. Passage of NH₃ into a solution of (I) yields a yellow diacetamido-compound, m. p. 153—154° after becoming red at 120°, which loses NH₃ when preserved over P₂O₅ and KOH and then becomes colourless. Treatment of (II) with Ac₂O in pyridine yields the compound C₃₃H₃₆O₁₆N₂; m. p. 177—178° after softening at 175°, [α]_D²⁰ -45.20° in CHCl₃, not readily hydrolysed and stable towards MeI and Ag₂O in COMe₂. 2-Hydroxy-2-glucosoxyanthraquinone-9-imine hydrate and BzCl in pyridine yield completely benzoylated alizarin-glucoside, m. p. 208° after softening at 156°, [α]_D²⁰ -32.72° in CHCl₃, obtained also from benzoglucosylalizarin. Methylation of (I) and 1-hydroxy-8-acetoglucosoxyanthraquinone-9-imine is accompanied by elimination of N and production of acetylacetoglucosylalizarin and 1-methoxy-8-acetoglucosoxyanthraquinone, respectively.

H. WREN.

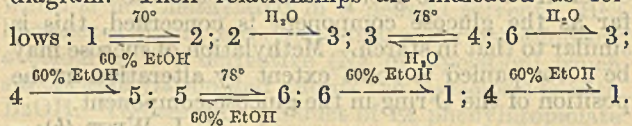
Dehydrogenation of sapogenin. Constitution and synthesis of sapotalin. E. SPÄTH and O. HROMATKA (Monatsh., 1932, 60, 117—128).—Dehydrogenation of sapogenin with Se at 300—340° gives sapotalin (18%) and unidentified hydrocarbons, m. p. 126—127°, b. p. 120°/0.0012 mm. (picrate, m. p. 161—163°), m. p. 116°, b. p. 170°/0.0012 mm. (picrate, m. p. 213—215°), m. p. 228—230.5° (sublimes about 210° in high vac.), and m. p. 304—305°. Sapotalin is oxidised by aq. KMnO₄ at 100° to trimellitic and mellophanic acids, whence it could be 1:2:6- (known), 1:4:6-, or 1:2:7-trimethylnaphthalene; it is shown to be the last-named by synthesis.

β -*p*-Tolylethyl bromide is condensed with CMeNa(CO₂Et)₂, and the resulting ester, b. p. 191—192°/14 mm., hydrolysed to β -*p*-tolylethylmethylmalonic acid, m. p. 160—161°, decarboxylated at 180° to γ -*p*-tolyl- α -methylbutyric acid (amide, m. p. 146—147°); the acid chloride with AlCl₃ in light petroleum gives 1-keto-2:7-dimethyl-1:2:3:4-tetrahydronaphthalene, b. p. 142—143°/16 mm. (semicarbazone, m. p.

204—206°). The last-named is condensed with MgMeI and the crude carbinol obtained dehydrated by Ac₂O at the b. p. to 1 : 2 : 7-trimethyl-3 : 4-dihydro-naphthalene, which is dehydrogenated by Pd-charcoal at 190—200° or by Se at 300° to 1 : 2 : 7-trimethyl-naphthalene, identical with sapotalin in all respects.

H. A. PIGGOTT.

α-Dextrin of Schardinger. M. ULMANN, C. TROGUS, and K. HESS (Ber., 1932, 65, [B], 682—686).—Simple treatment of α-amylose affords six modifications which differ from one another in Röntgen diagram. Their relationships are indicated as follows:



The transformations occur partly in solution, partly in course of heterogeneous decomp. Prep. (2) is probably identical with Schardinger's α-dextrin in which the presence of H₂O has been overlooked, whilst prep. (3) is probably the same as Miekeley's hydrate. The readiness with which the preps. are interconverted necessitates caution in judgment of compounds obtained from α-amylose by chemical action, since differences between initial and final material may simply be due to variation in separation and after-treatment of the "reaction product."

H. WREN.

Nitrates of starch. I. Nitrates of starch from potato starch. J. HACKEL and T. URBAŃSKI (Rocz. Chem., 1932, 12, 276—297).—The yield, N content, and viscosity of solutions of starch nitrates in COMe₂ increase with the concn. and relative quantity of HNO₃, and diminish with rise in temp. above 0°. As the duration of reaction is increased, the above vals. at first rise to a max., thereafter regularly falling. The solubility in EtOH and the N content of starch nitrate are reduced by boiling with H₂O. Starch nitrate pptd. by H₂SO₄ is less stable than that pptd. by H₂O. The highest degree of nitration is given by mixtures of HNO₃, H₂SO₄, and H₂O in which the mol. concns. of H₂SO₄ and H₂O are approx. equal. When the relative concn. of H₂SO₄ to HNO₃ is <1 : 9, nitration proceeds differently from that of cellulose, probably owing to solubility of starch nitrate in such mixtures.

R. TRUSZKOWSKI.

Oxycellulose and its identity with β-cellulose and cellodextrin. E. PATERNO (Atti R. Accad. Lincei, 1932, [vi], 15, 20—26).—A sealed note, dated Nov. 7, 1926. Various oxycelluloses, obtained by the action of different oxidising agents, and including β-cellulose and cellodextrin, are identical, although varying in degree of purity; all are sol. in the moist state in 8—10% NaOH solution to give colloidal solutions from which acids ppt. them as a transparent jelly. The different oxycelluloses and the so-called viscose hydrocelluloses, that from silk included, contain only a single oxycellulose, which is of paramount importance in the prep. of viscose silk. Analysis indicates that oxycellulose contains only a small proportion of oxidised groups C₆H₁₀O₆.

T. H. POPE.

Exhausted cellulose. E. PATERNO (Atti R. Accad. Lincei, 1932, [vi], 15, 17—20).—“Exhausted

cellulose,” prepared by repeated treatment of cellulose with 18% NaOH, is a pure product and, like cotton, yields rather more than the theoretical proportion of glucose on hydrolysis. Certain of the products classified as hemicelluloses are formed by the action of the air, especially in presence of H₂O or salts and, still more so, of alkali.

T. H. POPE.

Action of hydrogen fluoride on carbohydrates.

III. B. HELFERICH and O. PETERS (Annalen, 1932, 494, 101—106).—Cellan (A., 1930, 72) is methylated (Me₂SO₄ and aq. KOH) to a product (OMe about 44%), [α]_D +145.1° in CHCl₃, hydrolysed by 2% MeOH-HCl to a mixture of methylated methylglucosides; hydrolysis of the glucoside fraction, b. p. up to 110°/0.2 mm., with 5% aq. HCl gives a little 2 : 3 : 4 : 6-tetramethylglucose (I). The % condensations (determined by the diminution in reducing power) occurring when 2 : 3 : 4- and 2 : 3 : 6-trimethylglucoses, (I), and glucose are treated with anhyd. HF are 58, 59, 68, and 95, respectively. These results indicate that cellan is not built up uniformly from glucose residues. Dissolution of cellulose (II) in anhyd. HF and addition of anhyd. Et₂O (after 10 min.) gives an almost F-free product which is largely insol. (or slightly sol.) in H₂O; more prolonged treatment affords a product containing 3.9—4.7% F. Similar short treatment of glucosidyl fluoride (III) gives a H₂O-sol. product (8.1% F); the F content after more prolonged treatment is 7.4%. Fredenhagen's view (A., 1931, 1119) that (III) is produced from (II) and HF is criticised.

H. BURTON.

Cellulose sulphuric esters. II. W. TRAUBE,

B. BLASER, and E. LINDEMANN (Ber., 1932, 65, [B], 603—612; cf. A., 1928, 621).—Prolongation of the action of ClSO₃H on cellulose in presence of pyridine does not lead to the production of a homogeneous trisulphate, whereas esters with less than 3 SO₄H groups per C₆H₁₀O₅ cannot be isolated by the action of SO₃ on cellulose. In the last-named reaction it is advantageous to replace gaseous SO₃ by a solution of SO₃ in CS₂ and to use the cellulose in excess. The product is poured into an excess of KOH, unattacked cellulose is removed, and the filtrate worked up for the K₃ salt (cf. *loc. cit.*). The corresponding (NH₄)₃ salt is described. Addition of pyridine to the solution of SO₃ in CS₂ followed by evaporation of the latter and addition of cellulose gives an ester with 2.6 SO₄H groups. The esters obtained by the pyridine process (K and Na salts described) are more closely allied to cellulose than those obtained by means of SO₃, for which the nomenclature “hydrocellulose sulphates” is proposed. The viscosities of aq. solutions, Cu no., and [α]_D for the two series are recorded. The wide variation, particularly in viscosity, appears to indicate that the micellar structure of cellulose is not destroyed unless all the OH groups are replaced by the SO₄H residue. The behaviour of K hydrocellulose trisulphate as protective colloid and its inhibition of the pptn. of BaSO₄, HgCrO₄, and PbI₂ (properties shared by the “pyridine” sulphate) indicate a high mol. wt. confirmed by the non-elevation of the b. p. of H₂O, in which, however, it has marked electrical conductivity. H₃ hydrocellulose trisulphate is quantitatively hydro-

lysed by MeOH-HCl, which does not attack the K_2 salt.
H. WREN.

Relation of cellulose to lignin in wood. K. FREUDENBERG (Papier-Fabr., 1932, 30, 189—195).—The results of chemical, X-ray, and microscopical investigations indicate that cellulose is built up from glucose or cellobiose residues and lignin from coniferyl alcohol or phenolic residues in order to produce the structure of the wood fibre. There is no combination between cellulose and lignin, but the whole structure resembles reinforced concrete in that the cellulose micelles are held in position by lignin and hemi-cellulose.
B. P. RIDGE.

Basis for the physiological activity of -onium compounds. IX. Derivatives of homologues of betaine. R. R. RENSHAW and M. E. MCGREAL (J. Amer. Chem. Soc., 1932, 54, 1471—1474).—The following trialkyl-carbomethoxy- and -carbethoxy-methylammonium bromides are prepared from $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Me}(\text{Et})$ and the requisite trialkylamine: triethyl-carbomethoxy-, m. p. 132°, and -carbethoxy-, m. p. 104°; tri-*n*-propyl-carbomethoxy-, m. p. 138°, and -carbethoxy-, m. p. 134°; tri-*n*-butyl-carbomethoxy-, m. p. 113°, and -carbethoxy-, m. p. 83°; triisooamyl-carbomethoxy-, m. p. 99.5°; phenyldimethylcarbomethoxy-, m. p. 99°; benzyl dimethyl-carbomethoxy-, m. p. 151°, and -carbethoxy-, m. p. 114.5°; dibenzylmethyl-carbomethoxy-, m. p. 128°, and -carbethoxy-, m. p. 148°; methylammonium bromides. Triisooamylcarboxyanilido-, m. p. 169°, triethylcarboxy-, m. p. 190°, tri-*n*-propylcarboxy-, m. p. 177°, and triisooamylcarboxy-, m. p. 144°. -methylammonium bromides are also prepared. The $\cdot\text{CO}_2\text{H}$ compounds have no action on the autonomic nervous system; the activity of the esters varies with the different *N*-alkyl groups.
C. J. WEST (b).

Reactions between sugars and amino-acids. II. Syntheses of some amino-acid glucosides. K. MAURER and B. SCHIEDT (Z. physiol. Chem., 1932, 206, 125—132; cf. A., 1926, 602).—Tetra-acetylsarcosine ester glucoside with HCl in Et_2O gives the hydrochloride, m. p. 78°. Sarcosine amide glucoside with pyridine- Ac_2O affords the Ac_2 derivative, m. p. 176°, $[\alpha]_D^{25} +13.66^\circ$ in CHCl_3 . Treatment of sarcosylglycine with HCl in EtOH gives the *Et* ester (I), m. p. 88—89°; (I) condenses with acetobromoglucose to tetra-acetylsarcosylglycine ester glucoside, m. p. 125°, $[\alpha]_D^{25} +7.52^\circ$ in CHCl_3 . Sarcosine *Et* ester and acetobromocellobiose yield hepta-acetylsarcosine ester cellobioside, m. p. 164°, $[\alpha]_D^{25} -8.1^\circ$ in CHCl_3 (hydrochloride, m. p. 89°), which gives a syrupy amide glucoside with NH_3 in MeOH and on reacylation of the latter, octa-acetylsarcosine amide cellobioside, m. p. 254° (decomp.), $[\alpha]_D^{25} -11.43^\circ$ in CHCl_3 . (I) with acetobromocellobiose affords hepta-acetylsarcosylglycine ester cellobioside, m. p. 212°, $[\alpha]_D^{25} -8.32^\circ$ in CHCl_3 .
J. H. BIRKINSHAW.

Configurative behaviour of isoleucine in the Walden inversion. E. ABDERHALDEN and F. SCHWEITZER (Z. physiol. Chem., 1932, 206, 116—124).—dl- α -Bromo- β -methyl-*n*-valeryl derivatives of the NH_2 -acids: dl-leucine, m. p. 120—124° (sinters about 114°), -glycine, m. p. 120—122°, and *l*-tyrosine were not attacked by trypsin or yeast maceration juice.

The four optically active derivatives of leucine were obtained; d- α -bromo- β -methyl-*n*-valeryl-*d*-leucine, m. p. 128°, $[\alpha]_{\text{light}}^{18} +62.0^\circ$; d-*l*-, m. p. 157°, $[\alpha]^{18} +5.15^\circ$, l-*l*-, m. p. 128° $[\alpha]^{18} -62.1^\circ$; l-*d*-, m. p. 157°, $[\alpha]^{18} -5.03^\circ$ (all rotations in EtOH). The rate of elimination of Br by *N*-alkali was greater in the compounds containing components opposite in configuration (*l-d*- and *d-l*-). From this fact and the sp. rotation it is concluded that in the conversion of isoleucine into the corresponding α -bromo-fatty acid and in formation of the NH_2 -acid from the latter by amination there is no change in configuration.
J. H. BIRKINSHAW.

Determination of the ionisation constants of guanidine and its alkylated derivatives. T. L. DAVIS and R. C. ELDERFIELD (J. Amer. Chem. Soc., 1932, 54, 1499—1503).—The following new salts are reported: butylguanidine sulphate, m. p. 206°, nitrate, m. p. 69°, and picrate, m. p. 154.5°; heptylguanidine sulphate, nitrate, and picrate, m. p. 244° (decomp.), 86°, and 140.5°, respectively; benzylguanidine sulphate, nitrate, and picrate, m. p. 204°, 165°, and 185.5°; piperidoguanidine nitrate, m. p. 154° (decomp.); NN'-dimethylguanidine sulphate and nitrate, m. p. 264—265° and 68° (decomp.), respectively; NN'-diethylguanidine sulphate, m. p. 234—235° (decomp.); NN'-diamylguanidine sulphate and picrate, m. p. 190—191° (decomp.) and 108°, respectively; NN'N''-trimethylguanidine sulphate, nitrate, and picrate, m. p. above 345°, 276°, and 214.5°, respectively. The vals. of $K \times 10^{-4}$ are given for some of the guanidines; the basic strength of the alkylguanidines appears to be a function only of the positions of the substituents. Introduction of a Ph group into guanidine lowers the basicity. General details for the synthesis of amines are given in the prep. of heptylamine.
C. J. WEST (b).

β -Halogenes. XIX. 1. Action of halogen on fulminic acid and fulminates. 2. Trihalogeno-nitrosomethanes. L. BIRCKENBACH and K. SENNEWALD (Ber., 1932, 65, [B], 546—552; cf. this vol., 505).—Hg fulminate in aq. suspension is converted by Cl_2 into dichloroformoxime (I) (40%) and dichlorofuroxan, whereas the latter substance is almost quantitatively obtained in EtCl at -80° . The yields of dibromofuroxan and dibromoformoxime (II) from Hg fulminate and Br in H_2O , *N*- H_2SO_4 , and 5*N*- H_2SO_4 are 30% and 25%, respectively. (I) in 50% EtOH gives di-iodofuroxan in 90% yield. The course of the reaction of halogen and Hg fulminate in presence of halogen acid [not mineral acids as stated by Endres (this vol., 257)] is governed by the liberation of fulminic acid, and not by hydrolysis of the primary product $[\text{CHal}_2\text{N}\cdot\text{O}]_2\text{Hg}$ in acid medium.

Dichlorobromonitrosomethane, b. p. 21°/24 mm., obtained by successive addition of Br and NaOAc to (I) in H_2O , is transformed by Br into dichlorodibromomethane, b. p. 135°, and reduced by H_2S in MeOH to (I). $\text{CBr}_3\cdot\text{NO}$, b. p. 34—39°/14 mm., prepared by addition of Na fulminate to NaOAc and Br in dil. AcOH, is transformed by hot H_2O into CHBr_3 and CBr_4 . (II), treated successively with HgCl_2 , Br, and NaOAc, affords chlorodibromonitrosomethane, b. p. 24°/20 mm., passing into CClBr_3 , b. p. 158—159.5°, m. p. 55°, when heated with Br. Dibromoformoxime

hydrate, m. p. 40°, prepared in 80% yield from Na fulminate and Br in presence of 20% H₂SO₄, gives *chlorobromoformoxime*, m. p. 36°, when treated with HgCl₂ in H₂O. Addition of Na fulminate to (I) suspended in EtOH and conc. H₂SO₄ afford *di-iodoformoxime hydrate*, m. p. 52°. H. WREN.

Alkylation of nitriles in liquid ammonia. J. B. CLOKE (J. Amer. Chem. Soc., 1932, 54, 1690—1691).—The alkylation of nitriles in liquid NH₃ reported by Nieuwland and Baldinger (this vol., 382) has been previously observed by the author (A., 1931, 1031). C. J. WEST (b).

Configuration of simple amino-nitriles and diamines. H. REIHLEN, E. WEINBRENNER, and G. VON HESSLING (Annalen, 1932, 494, 143—158).—(—)-*l*-α-Aminopropionitrile (I), [M]_D²⁰ -18.4° in H₂O (cf. Delépine, A., 1904, i, 148) [*H tartrate* (+H₂O), [M]_D²⁰ +23.2° in H₂O], is hydrolysed by cold conc. HCl to the hydrochloride, [M]_D²⁰ +13.1° in H₂O, of (+)-*l*-α-aminopropionamide, [M]_D²⁰ +7.2° in H₂O. The (—)-*Ac* derivative (II), m. p. 102°, of (I) is reduced catalytically (PtO₂) in Ac₂O (cf. this vol., 256) to (—)-*l*-α-*diacetamidopropane*, m. p. 153°, [M]_D²⁰ -64° in EtOH, hydrolysed by conc. HCl to (+)-*l*-α-*propylenediamine*. Reduction (H₂-PtO₂) of (II) in EtOH and subsequent benzylation gives (—)-*l*-α-*benzamido-β-acetamidopropane*, m. p. 163°, whilst similar reduction (in Ac₂O) of the Bz derivative, m. p. 128° (lit. 123.5°), of (I) affords (—)-*l*-β-*benzamido-α-acetamidopropane*, m. p. 187°. Phenylethylenediamine is resolved by *d*-tartaric acid into *l*-, b. p. 104°/1—2 mm., m. p. 4—5°, [M]_D²⁰ -47.8° [*tartrate*, m. p. 220° (decomp.), [M]_D²⁰ +116.6° in H₂O]; (—)-*Ac*₂, m. p. 174°, and (—)-*Bz*₂, m. p. 227°, derivatives], and *d*-forms [*H tartrate*, m. p. 180° (decomp.), [M]_D²⁰ +29° in H₂O]. α-Aminophenylacetonitrile is partly resolved through its *H tartrate* to the *l*-form [(—)-*Ac* derivative, m. p. 130.5°, [M]_D²⁰ -23° in CHCl₃], the (+)-*Bz* derivative, m. p. 151°, [M]_D²⁰ +8° in CHCl₃, of which is reduced (H₂, PtO₂, Ac₂O) to (—)-β-*benzamido-α-acetamido-β-phenylethane*, m. p. 190—193°. The configurations (denoted by *l*) assigned to the derivatives of α-aminophenylacetic acid are determined essentially by Freudenberg and Rhino's method (A., 1924, i, 1173). In the above cases (±) represents the sign of rotation. Vals. of [M]_D²⁰ for the *Ac* and *Bz* derivatives of the *d*-series of the above NH₂-compounds and NH₂-CHPhMe in various solvents are recorded.

H. BURTON.

Aliphatic germanium derivatives. I. Triethylgermanium compounds; their properties and reactions. C. A. KRAUS and E. A. FLOOD. II. Diphenyldiethylgermane, germanium diethyl oxide, and germanium diethyl dibromide. E. A. FLOOD (J. Amer. Chem. Soc., 1932, 54, 1635—1644, 1663—1667).—I. GeEt₃ is obtained in 91% yield from GeBr₄ and MgEtBr. Addition of a 50% solution of Br in EtBr to GeBr₄ during 6 days gives 82% of *Ge Et₃ bromide*, b. p. 190.9°/760 mm., f. p. -33°, hydrolysed to *Ge Et₃ oxide*, (GeEt₃)₂O, b. p. 253.9°, which is stable towards oxidation, is converted by halogen acids into GeEt₃X, and with Li in NH₃Et gives (probably) a mixture of LiGeEt₃ and LiO·GeEt₃. *Ge Et₃ fluoride*, b. p. 149°/751 mm., *chloride*, b. p.

175.9°, and *iodide*, b. p. 212.3°, are described; the fluoride is more stable towards hydrolysis than the other halides. GeEt₃Br and liquid NH₃ afford a 1:1-*compound* having a v. p. of 10 mm. at room temp. GeEt₃Br is ammonolysed in liquid NH₃; the lower liquid phase formed in the reaction contains *diethylgermaniumimine*, b. p. about 100°/0.1 mm., which reacts with H₂O to form the oxide. The halides react with Li in NH₂Et to give (GeEt₃)₂ (not a satisfactory method of prep.); GeEt₃Br and Na heated at 210° for 12 hr. and then at 270° during 5 days, give *hexaethylgermane* (I), b. p. 265°/758 mm. (I) and Br in EtBr give GeEt₃Br; with Na in liquid NH₃ no appreciable reaction occurs, whilst with Li in NH₂Et LiGeEt₃ [which ammonolyses (more completely in NH₃) to GeHEt₃ and LiNH₂ (or LiNH₃)] results; if NH₃ is passed into the reaction vessel after removal of the NH₂Et, *triethylgermane*, b. p. 124.4°/751 mm., is obtained. This decolorises Br in EtBr, does not react with Na in liquid NH₃, and gives H₂ with KNH₂. (I) and K in NH₂Et give *K triethylgermane*, which with EtBr affords GeEt₄.

II. GePh₂Br₂ and MgEtBr in Et₂O give 95% of *diphenyldiethylgermane*, b. p. 316°, converted by Br in *s*-C₂H₄Br₂ into PhBr and GeEt₂Br₂. Hydrolysis of the product from GeEt₃F and Br in EtBr with NaOH give *Ge Et₂ oxide*, amorphous, m. p. 175°, and unstable liquid (termol.) forms; the latter (f. p. about 18°) is transformed into the solid at room temp. in a few hr., the process being accelerated by a trace of H₂O; transition between the two forms occurs about 110°. The oxide and HBr give *Ge Et₂ dibromide*, b. p. 202°, hydrolysed to the oxide and converted by liquid NH₃ into *diethylgermaniumimine*, b. p. 100°/0.01 mm. C. J. WEST (b).

cycloPropane hydrocarbons: general methods of preparation. R. LESPIEAU and R. L. WAKEMAN (Bull. Soc. chim., 1932, [iv], 51, 384—400).—Hexane-βδ-diol and PBr₃ give βδ-*dibromohexane*, b. p. 81.5—83°/10 mm., debrominated with Zn and EtOH to 1-*methyl-2-ethylcyclopropane*, b. p. 63.9—64.9°. βδ-Dibromo-βδ-dimethylpentane, prepared from the corresponding diol, similarly affords a small yield of 1:1:2-*trimethyl-2-ethylcyclopropane*, b. p. 103.5—104.5°. γ-*Bromo-αγ-diphenyl-Δ^β-propene*, m. p. 54—54.5° (*dibromide*, m. p. 130.5—131.5°), gives αγ-*dibromo-αγ-diphenylpropane*, debrominated to 1:2-*diphenylcyclopropane*, b. p. 164—166°/13 mm. (cf. Kishner, A., 1915, i, 952). MgPrBr and β-*bromobutaldehyde*, b. p. 42—44°/12 mm., afford β-*bromohexan-δ-ol*, b. p. 99—101°/10 mm., which forms with HBr βδ-*dibromohexane*, b. p. 99—100°/12 mm., debrominated to 1-*methyl-2-propylcyclopropane*, b. p. 92—93°. For determination of the amount of olefine present in the cyclic hydrocarbons, reaction with KBr-KBrO₃ gives good results. The general methods of prep. of cyclopropane hydrocarbons are discussed.

F. R. SHAW.

Bromination of organic compounds in presence of activated charcoal. L. A. NIKOLAEV (J. Gen. Chem. Russ., 1931, 1, 1035—1038).—Freshly ignited animal charcoal first treated with Br and then with C₆H₆ causes rapid formation of PhBr and *p*-C₆H₄Br₂, although there is no action with Cl₂

or I. Similarly, from EtOH and Br, EtBr, ethylene dibromide, and a lachrymatory oil, b. p. 128°, are obtained; Cl₂ and I do not react with EtOH in presence of charcoal. It is suggested that in spite of being rapidly absorbed by charcoal, Cl₂ is incapable of bringing about the polarisation of a non-polar mol. such as C₆H₆, being less activated than Br. Activated Br has a more powerful polarising effect owing to its greater residual valency and also reacts more rapidly with polar mols. G. A. R. KON.

Polymethylbenzenes. V. Separation of mesitylene from ψ -cumene. VI. Separation of durene from isodurene. VII. Jacobsen reaction. II. L. I. SMITH and O. W. CASS (J. Amer. Chem. Soc., 1932, 54, 1603—1609, 1609—1614, 1614—1621).—V. Xylene, MeCl, and AlCl₃ give a mixture of trimethylbenzenes [also obtained in about 15% yield from xylene (4 pts.) and AlCl₃ (1 pt.) at 130—140°] containing no 1:2:3-derivative. Sulphonation of the mixture and treatment of the mixed sulphonic acids with HCl (const. b. p.) at 80° causes hydrolysis of mesitylenesulphonic acid (I) (+2H₂O), m. p. 78°, m. p. (anhyd.) 98.5—100°, to mesitylene (II) which is removed by steam-distillation at 80° under reduced pressure [in order to obtain pure (II) the above processes must be repeated]. ψ -Cumene-5-sulphonic acid (III) (+1.5H₂O), m. p. 111—112°, m. p. (anhyd.) 128—131°, separates from the reaction mixture after removal of (II), and is converted into ψ -cumene (IV) by steam-distillation from 50% H₂SO₄ at 135—145°. Pure (III) can be obtained from a mixture of (I) and (III) by washing with CHCl₃, whereby (I) is removed, but cannot be isolated pure. The refractive index of a mixture of (II) and (IV) is a linear function of the composition.

VI. The mixture of tetramethylbenzenes produced in the above methylation is cooled to -15°, whereby durene (V) [sulphonic acid (+2H₂O), m. p. 113°] separates. The filtrate from this contains isodurene (VI) [sulphonic acid (+2H₂O), m. p. 79°] saturated with (V); prehnitene [sulphonic acid (+2H₂O), m. p. 104°] is not present. Details are given for the separation of (V) and (VI) from the above filtrate; the method involves fractional sulphonation and hydrolysis.

VII (cf. A., 1929, 1433). The Jacobsen reaction occurs either (a) by the shift of Me (alkyl) groups from mol. to mol., giving higher and lower methylated benzenes, or (b) by internal rearrangement of Me groups to a system more stable towards H₂SO₄ or other strong dehydrating agents. Of the polymethylbenzenes, only (V), (VI), and C₆HMe₅ (VII) undergo the reaction; (V) and (VI) react according to (b), giving prehnitene (VIII), whilst (VII) reacts according to (a), giving (VIII) and C₆Me₆. Mixtures of (V) and (VI) can thus be used in the prep. of (VIII). By-products of the reactions are SO₂, black H₂O-sol. material, and brown amorphous H₂O-insol. material, the last constituting 10—30% of the total materials recovered. Rearrangement of the sulphonic acid (not the hydrocarbon) occurs; the dehydrating agent (P₂O₅ or H₂SO₄) is necessary, since the acids alone are stable. The shift of the Me groups is accompanied by reduction of the sulpho-group of part of the material

used. The orientation effects of the Jacobsen reaction and those of direct methylation of C₆H₆ hydrocarbons are entirely opposite in the case of tetramethylbenzene. C. J. WEST (b).

Polymerides from benzyl chloride and related compounds. R. A. JACOBSON (J. Amer. Chem. Soc., 1932, 54, 1513—1518).—CH₂PhCl is polymerised by a little AlCl₃ to (mainly) an insol. hydrocarbon (C₇H₈)_x and a small amount of a sol. resin of the same empirical formula. The proportions of these are reversed when FeCl₃ is used, whilst with SnCl₄, the sol. polymeride results. The mol. wt. of the sol. resin is 1260—2250. The polymerides are not readily attacked by oxidising agents. Polymerisation of *p*-C₆H₄Br·CH₂Cl proceeds similarly; the unit of both the insol. and sol. polymerides is C₇H₅Br and the mol. wt. of the resin varies from 1300 to 1500. Polymerides have been obtained from *p*-C₆H₄Br₂ and *p*-C₆H₄(CH₂Br)₂ by the Wurtz reaction; the former gives a sol. polymeride, whilst the latter affords an infusible insol. polymeric hydrocarbon (C₈H₈)_x. C. J. WEST (b).

Diphenyl and its derivatives. XI. New derivatives of 2-methyldiphenyl and influence of methyl on reactions of the amino-group in the 2'-position. L. MASCARELLI and D. GATTI [with P. LAVAZZA] (Atti R. Accad. Lincei, 1932, [vi], 15, 89—91; cf. this vol., 509).—2-Nitro-2'-methyldiphenyl, m. p. 57—58°, was prepared from *o*-iodotoluene, *o*-iodonitrobenzene, and Cu. 2-Amino-, m. p. 37°, b. p. 157—158°/17 mm. (hydrochloride, m. p. 128°, decomp. 130—131°), 2-chloro-, b. p. 174°/50 mm., 276°/755 mm., 2-bromo-, b. p. 285—286° (decomp.) or 156—157°/27 mm., 2-iodo-, m. p. 38—39°, b. p. 186—187°/30 mm., and 2-cyano-, b. p. 213—214°/63 mm., 2'-methyldiphenyl were prepared. The formation of no compounds (carbazole, diphenylene oxide, idonium base) indicating closure (by means of NH, O, I) of a third nucleus on the 2:2'- or 2:6'-position was observed. Hence, not only is the 2-Me not expelled during the diazo-reaction and subsequent decomp. of the diazo-compound by means of H₂O, CuCl(Br), or KI, but it does not disturb the reactions of the 2'-NH₂-group. T. H. POPE.

Variations in the behaviour of phenyl-ethylenes and -ethanes during catalytic hydrogenation. W. H. ZARTMAN and H. ADKINS (J. Amer. Chem. Soc., 1932, 54, 1668—1674).—Increase in the no. of Ph groups in the phenylethylenes increases the temp. and/or pressure required for hydrogenation to the corresponding phenyl- and cyclohexyl-ethanes and decreases the rate of hydrogenation under comparable conditions. The increased difficulty of hydrogenation with rise in mol. wt. is not large, since CPh₂:CPh₂ is converted into the ethane at 100°, and CPh₃:CHPh₂ into pentacyclohexylethane at 125°, at reasonably rapid rates. The successive substitution of Ph groups in C₂H₄ materially lowers the stability of the C-C linking, so that when three Ph groups are in the mol. the ethane can be cleaved at 200° over a Cu-Cr oxide catalyst. CPh₃:CHPh₂ undergoes fission over Ni at 125°. The labilising effect (if any) of cyclohexyl groups on the ethane C atoms is very small, since pentacyclohexylethane is

stable at 200° over Ni or Cu-Cr oxide catalysts. $\alpha\alpha\beta$ -Tricyclohexylethane, b. p. 191—192°/8 mm., $\alpha\alpha\alpha\beta$, m. p. 112—114°, and $\alpha\alpha\beta\beta$ -tetracyclohexylethane, m. p. 158—159°; β -phenoxy- α -diphenylethane, b. p. 214—217°/8 mm., m. p. 64—65°; pentacyclohexylethane, m. p. 191—192°, and β -phenoxy- α -diphenylethylene, b. p. 235°/23 mm., m. p. 58—59°, are incidentally described. Data are given for the reduction of styrene, stilbene, tri- and tetra-phenylethylenes, β -phenoxy- α -diphenylethylene, $\alpha\alpha$ - and $\alpha\beta$ -di- and penta-phenylethanes, and also the cleavage products of several of these compounds.

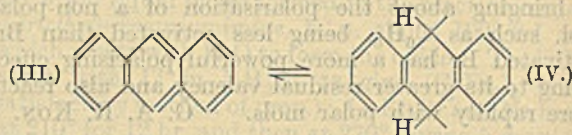
C. J. WEST (b).

Syntheses of alkylphenanthrenes. I. 1-, 2-, 3-, and 4-Methylphenanthrenes. R. D. HAWORTH (J.C.S., 1932, 1125—1133).—Reduction of β -1- and β -2-naphthoylpropionic acids (prep. described) by Clemmensen's method and cyclisation with 85% H_2SO_4 affords 1- (I) and 4-keto-1:2:3:4-tetrahydrophenanthrene. MgMeI and (I) afford a carbinol (picrate, m. p. 127—128°) [the 4-keto-compound affords 4-hydroxy-4-methyl-1:2:3:4-tetrahydrophenanthrene, m. p. 111—112° (picrate from cold MeOH, m. p. 96—98°, from hot MeOH, m. p. 110°)]. Either carbinol when dehydrated with HCO_2H at 100° and then treated with Se affords 1-methylphenanthrene, m. p. 118° (picrate, m. p. 135—136°; quinone, m. p. 191°), and 4-methylphenanthrene, m. p. 49—50° (lit. 117°) [picrate, m. p. 140—141° (lit. 125°); quinone, m. p. 187°; quinoxaline, m. p. 178°]. 1-Keto- and 4-keto-1:2:3:4-tetrahydrophenanthrene afford with $(\text{CO}_2\text{Et})_2$ and KOEt , *Et* 1-keto-1:2:3:4-tetrahydrophenanthrene-2-glyoxylate (I), m. p. 84—85°, and *Et* 4-keto-1:2:3:4-tetrahydrophenanthrene-3-glyoxylate, m. p. 75—76°, also prepared by cyclisation of γ -1-naphthyl- α -methylbutyric acid with 85% H_2SO_4 . Reaction of C_{10}H_8 with methylsuccinic anhydride in PhNO_2 containing AlCl_3 affords β -2-, m. p. 165—166°, and β -1-naphthoyliso-butyric acid, m. p. 123—124°, which are reduced to γ -2-naphthyl- α -methylbutyric acid, m. p. 85—86°, converted by H_2SO_4 into 4-keto-3-methyl-1:2:3:4-tetrahydrophenanthrene, m. p. 64—65°, and thence into 3-methylphenanthrene, m. p. 62—63° (lit. 65°) [picrate, m. p. 137—138° (lit. 141°); quinone, m. p. 205—206°; quinoxaline, m. p. 207—208°], by reduction and dehydrogenation, and γ -1-naphthyl- α -methylbutyric acid, m. p. 90°, cyclised by H_2SO_4 to 1-keto-2-methyl-1:2:3:4-tetrahydrophenanthrene and thence to 2-methylphenanthrene, m. p. 55—56° (lit. 52—53°) (picrate, m. p. 118—119°; quinone, m. p. 147—148°; quinoxaline, m. p. 186—188°).

J. L. D'SILVA.

Polynuclear aromatic hydrocarbons. XII. Distribution of the double linkings in condensed aromatic hydrocarbons. E. CLAR (Ber., 1932, 65, [B], 503—519; cf. A., 1931, 1282, 1292).—The absorption spectra of the following compounds are described: 2:3:6:7-dibenzanthracene-9:10-diyl (I) and its 9:10- Cl_2 -derivative; 2:3-benzanthracene (II); 1:2:3:4-dibenzanthracene; 2':3'-naphtha-2:3-phenanthrene; 2':1'-anthraceno-1:2-anthracene; 7:7'-dimethyl-2':3'-naphth-1:2-anthracene. The formation of the first bands in the region of longer wave-length in the case of anthracene derivatives

(A bands) is attributed to unpaired electrons of the *meso*-C atoms. This condition (*R* state), in which these C atoms possess electron septets, is in equilibrium with the *o*-quinonoid state ($\text{III} \rightleftharpoons \text{IV}$). $\text{Log } \epsilon_{\text{max}}$ of the A bands, and consequently the % content of



the anthracenes in the *R* state, increases with increasing reduction potential of the *o*-quinones from which the anthracenes are evolved, and conversely. The displacement of the first A bands in comparison with those of anthracene is a measure of the valency demand of the *o*-arylene residues. In polynuclear aromatic hydrocarbons of the anthracene type, the *o*-arylene residues replacing the *o*-phenylene group of anthracene are so united to the central ring that the union in the *R* state is formed by a double linking. The structure of the naphthylene residue is unsymmetrical in linear, symmetrical in angular, union.

(I) and PCl_5 in boiling $\text{C}_6\text{H}_4\text{Me}_2$ yield an additive product which passes into 9:10-dichloro-2:3:6:7-dibenzanthracene-9:10-diyl, decomp. 305° when rapidly heated, oxidised by air in sunlight to 2:3:6:7-dibenzanthraquinone. It reacts slowly with *p*-benzoquinone, very rapidly with maleic anhydride. (II), m. p. 341°, prepared by distilling tetrahydro-2:3-benzanthraquinone over Zn dust and Cu powder, reacts more readily than anthracene with maleic anhydride in boiling $\text{C}_6\text{H}_4\text{Me}_2$, and is smoothly oxidised by air in ultra-violet light to 2:3-benzanthraquinone. 9:9'-Dianthryl has m. p. 308—310°; 9:10-endo-2:3-benzanthracene-, m. p. (indef.) 273—282° (decomp.), and 9:10-endo-1:2-benzanthracene-, m. p. 242°, $\alpha\beta$ -succinic anhydride are described.

H. WREN.

N-Chlorosulphonyl-amides and -sulphonamides. Reactivity of sulphuryl chloride. J. MEYBECK (Ann. Chim., 1932, [x], 17, 129—206).—Action of SO_2Cl_2 on sodioformanilide (improved prep.) gives *N*-chlorosulphonylformanilide (I), m. p. 80—81° (yield 27.4%). Similarly are obtained *N*-chlorosulphonylacetanilide (II), m. p. 71° (yield 30%) (together with a little *p*-chloroacetanilide), and *benzanilide* (III), m. p. 109.5—110° (yield 10—15%), also obtained from the K derivative (yield 33%), from the product of interaction of MgEtBr and NPhBz (together with Br) (yield 9%), and from the similar product using MgPrCl (yield 58%); *N*-chlorosulphonyl-*p*-toluenesulphonanilide (IV), m. p. 138.5—139° (yield 23%), *o*- (V), m. p. 107.5—108° (yield 20%), *p*- (VI), m. p. 106.5—107.5°, and *m*-toluidide (VII), m. p. 125.5—126°. These substances when heated with Cu evolve SO_2 and give unidentified products [from (II) a substance, m. p. 180—185°, is obtained]. With conc. H_2SO_4 HCl is evolved. Hydrolysis with H_2O , acids, or alkalis gives the original anilides, except (I), which with NaOH gives PhNC , whilst (II) gives NH_2Ph . With NaOH in $\text{EtOH-H}_2\text{O}$ at room temp. sulphamates are probably formed, e.g., $\text{NPhBz}\cdot\text{SO}_3\text{Na}$. The action of heat gives SO_2 , HCl , and unidentified products, AcCl and BzCl being formed from (II) and (III),

respectively. (II) with EtOH gives EtOAc and HCl. (I) and (III) react similarly, whilst (IV), (V), (VI), and (VII) are unattacked. Interaction of sodio-*p*-toluenesulphonamide and (IV) gives a substance, m. p. 195—197°. NH₂Ph and (IV) give NH₂Ph.HCl, *p*-toluenesulphonamide, and coloured products, similar products being obtained from (VI) together with (?) sulphondianilide (cf. this vol., 261). (VI) with NH₃ gives (?) sulphamide and trisulphimide, (SO₂.NH)₃, whilst with *o*-phenylenediamine 2:3-diaminophenazine is formed. The action of SO₂Cl₂ on formanilide, acetanilide, benzanilide, and *p*-toluenesulphon-anilide and *o*-toluidide in CCl₄ and CHCl₃ gives chlorinated anilides. A. A. LEVI.

p-Aminophenylguanidine: preparation of the nitrate, hydrochloride, and sulphate, and attempted preparation of the free base. C. E. BRAUN (J. Amer. Chem. Soc., 1932, 54, 1511—1513). —*p*-Aminophenylguanidine hydriodide and AgNO₃ in H₂O give 30.1% of the nitrate, m. p. 189—190°. *p*-Phenylenediamine and *S*-ethylisothiocarbamide hydrochloride in H₂O give 15% of *p*-aminophenylguanidine hydrochloride, m. p. 167—168.5°; the sulphate, decomp. 279°, is prepared similarly. The sulphate and aq. Ba(OH)₂ give (probably) the amorphous dihydrate, m. p. 182° (decomp.), of the free base, which when heated above 100° gives NH₃ and *p*-C₆H₄(NH₂)₂. C. J. WEST (b).

Stereochemistry of derivatives of ethane. III. Stereochemical course of ring fission of αβ-diphenylethyleneimines. A. WEISSBERGER and H. BACH (Ber., 1932, 65, [B], 631—636; cf. this vol., 259).—Addition of HCl to *dl*-*cis*-, *dl*-*trans*-, *l*-*trans*-, and *d*-*trans*-αβ-diphenylethyleneimine yields quantitatively *dl*-*iso*-, *dl*-, *l*-, and *d*-β-chloro-α-aminodibenzyl, respectively. Ring fission leads stereochemically exclusively to the chloroaminodibenzyls from which the imines are derived. Addition of the elements of H₂O to the *dl*-*cis*-, *dl*-*trans*-, *l*-*trans*-, and *d*-*trans*-imines in presence of 2*N*-H₂SO₄ gives mainly *dl*-*iso* with little *dl*-, mainly *dl*- with little *dl*-*iso*-, mainly *l*- with little *l*-*iso*-, and mainly *d*- with little *d*-*iso*-α-amino-β-hydroxydibenzyl, respectively. Racemisation is not observed. All the changes are mixtures of *cis*- and *trans*-addition. It is considered that only one C:N linking is ruptured during ring fission. *iso*-α-Acetamido-β-acetoxydibenzyl has m. p. 145—146° (corr.). H. WREN.

Alkylation of orange-I. A refutation. K. H. T. PFISTER (J. Amer. Chem. Soc., 1932, 54, 1521—1526).—A criticism of the work of Slotta and Franke (A., 1931, 344). Alkylation of orange-I is normal; the methylation, ethylation, propylation, butylation, and hexylation products are described. The Na salt (+2H₂O) of the Me ether has no val. as an indicator. The ethers are readily hydrolysed by acids, especially at higher temp. The use of HCl by Slotta and Franke probably resulted in the regeneration of the original material. C. J. WEST (b).

Configuration of phthalylbenzidine. E. E. TURNER (J.C.S., 1932, 1294—1295).—Contrary to Gugliamelli and others (this vol., 171), phthalylbenzidine (I) (prep. from benzidine phthalate described) can be

diazotised and coupled with β-naphthol, and dissolution in 1% NaOH affords the Na salt of the phthalamic acid, NH₂.C₆H₄.C₆H₄.NH.CO.C₆H₄.CO₂H, which is obtained by acidification of the NaOH solution. (I) is therefore *N*-4-(4'-aminodiphenyl)phthalimide (A., 1926, 1131) and does not possess the structure based on the Kaufler formula. J. W. BAKER.

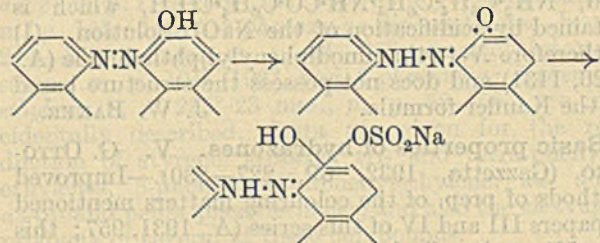
Basic properties of hydrazones. V. G. OTTO-LINO (Gazzetta, 1932, 62, 227—230).—Improved methods of prep. of the colouring matters mentioned in papers III and IV of this series (A., 1931, 957; this vol., 51) are described. E. E. J. MARLER.

Action of diazo-compounds on unsaturated compounds. VII. A new case of anomalous coupling. A. QUILICO and M. FRERI (Gazzetta, 1932, 62, 253—264).—Addition of *p*-propenyldimethylaniline, *p*-dimethylaminobenzaldehyde, or *pp*'-tetramethyldiaminobenzhydrol to EtOH suspensions of diazonium salts results in elimination of the side-chain, which is replaced by the group N₂R giving *p*-azo-derivatives of NPhMe₂. An explanation of the mechanism is given. E. E. J. MARLER.

Azo-sulphites of disazonaphthols and their fission into the corresponding aminoazo-naphthols. A. T. KING (J.C.S., 1932, 1265—1271).—Extension of azo-sulphite formation (A., 1927, 1180) to disazo-dyes of the type XN:N.Y.N:N.C₁₀H₆.OH (β) (X and Y=aromatic nuclei) permits the stabilisation of one azo-linking towards reducing agents, the unprotected azo-linking suffering fission either by the action of NaHSO₃ itself or by suitable reduction, with the formation of monoazo-dyes with an NH₂ group at the point of fission. By reactions of this type, the following are obtained, the disazo-sulphite usually being obtained at 0° in the presence of pyridine, fission to the mono-azo-derivative occurring at 60°. 2-Hydroxy-1-naphthaleneazo-*m*-tolueneazobenzene-*m*-trimethylammonium chloride with 5% NaHSO₃ at 60° gives its sulphite, converted by Na₂S₂O₄ into Na *p*-amino-*m*-tolueneazo-β-naphthol (Ac derivative, m. p. 251°); Na diphenyldisazo-4-sulpho-α-naphthylamine-8-sulpho-, converted into Na 4'-aminodiphenylazo-8-sulpho- (and 4'-aminodiphenylazo-β-naphthol-8-sulphonic acid); Na diphenyldiazo-4:8-disulpho-α-naphthol-8-sulpho-; Na diphenyldisazosalicylic acid-3:6-disulpho- and Na 4'-aminodiphenylazo-3:6-disulpho-; Na *p*-sulphobenzeneazobenzeneazo-8-sulpho-; Na monosulpho-4-amino-α-naphthaleneazo-α-naphthaleneazo-6-sulpho-; Na diphenyldisazophenetole-6:8-disulpho-; Na 4'-aminodiphenylazo-6:8-disulpho-; Na diphenyldisazo-3:6:8-trisulpho-α-naphthol-; Na 4'-aminodiphenylazo- [and 4'-aminodiphenylazo-β-naphthol (Ac derivative, m. p. 275°)]; Na ditolyldisazo-3:6:8-trisulpho-α-naphthol-; and Na *p*-aminoditolylazo-β-naphthol [reduced to *p*-aminoditolylazo-β-naphthol (Ac derivative, m. p. 233°)]-β-naphthyl sulphite. J. W. BAKER.

Sulphites of azo-compounds containing two hydroxyls. A. T. KING (J.C.S., 1932, 1271—1275).—Contrary to Voroschtsov's view (A., 1916, i, 293) dyes containing one azo-linking and two naphtholic OH groups do not give disulphites, since assump-

tion of the ketonised form by one of the β -naphthol nuclei automatically prevents the other from so doing :



This supports the hydrazone as opposed to the azo-structure for such compounds. Thus *Na* 4-sulpho-2-hydroxy- α -naphthaleneazo-, *Na* 4-sulpho-5-nitro-2-hydroxy- α -naphthaleneazo-, and *Na* 5-sulpho-2-hydroxy-benzeneazo- β -naphthyl sulphite are obtained. These are stable in NaHSO_3 solution at 60° , and at 70° are reconverted into the original dye, no fission taking place (cf. preceding abstract). On the other hand, disulphites are formed from disazo-compounds containing two β -naphthol nuclei, and thus *Na* diphenyl-disazobis-8-sulpho-, and *Na* 2:5:2':5'-tetramethyl-triphenylmethane-4:4'-disazobis-3:6-disulpho- β -naphthyl disulphites are obtained, although *Na* 2:2'-disulphodiphenyldisazobis- β -naphthol affords only a monosulphite. The significance of these results and those in the preceding abstract relative to SO_2 faults in dyed fabrics is discussed. J. W. BAKER.

A reaction of fluorene. A. J. HALLWOOD and R. ROBINSON (J.C.S., 1932, 1292—1293).—Fluorene condenses with PhNO_2 in presence of Na in xylene at 100° to give fluorenylideneaniline oxide, probably (I)

$\text{C}_6\text{H}_4 \begin{matrix} \uparrow \\ \text{C} \end{matrix} \begin{matrix} \text{N} \\ \text{Ph} \end{matrix}$, m. p. 193° , hydrolysed by boiling 40% H_2SO_4 to fluorenone and $p\text{-NH}_2\text{C}_6\text{H}_4\text{OH}$, and reduced by $\text{Na}_2\text{S}_2\text{O}_4$ in EtOH to fluorenylaniline, m. p. $122\text{--}123^\circ$ (*Ac*, m. p. 177° , and nitroso-, m. p. 104° , derivatives), also obtained from fluorenyl chloride and NH_2Ph with anhyd. NaOAc in *iso*- $\text{C}_6\text{H}_{11}\text{OH}$.

J. W. BAKER.

Resolution of 2-aminocyclohexanol. R. M. GODCHOT and M. MOUSSERON (Compt. rend., 1932, 194, 981—983).—2-Aminocyclohexanol (A., 1903, i, 680) is regarded as the *trans*-isomeride. Fractional crystallisation from EtOH of the *d*-tartrate of the *dl*-base, m. p. $152\text{--}153^\circ$, $[\alpha]_D +17.25^\circ$, affords the *d*-tartrate of *l*-*trans*-2-aminocyclohexanol, m. p. $177\text{--}178^\circ$, $[\alpha]_D -2.73^\circ$, and the *d*-tartrate of *d*-*trans*-2-aminocyclohexanol, m. p. $170\text{--}171^\circ$, $[\alpha]_D +31.2^\circ$. KOH liberates the *d*- and *l*-bases, m. p. $83\text{--}84^\circ$, $[\alpha]_D \pm 40.2^\circ$ (hydrochlorides, m. p. $147\text{--}148^\circ$, $[\alpha]_D \pm 31.60^\circ$). Catalytic reduction of *o*-amino- and *o*-acetamido-phenol yields cyclohexylamine and acetylcyclohexylamine and not *cis*-2-aminocyclohexanol.

J. L. D'SILVA.

Formation of *cis-cis*-muconic acid and benzoquinone in the oxidation of phenol with peracetic acid. J. BÖESEKEN and R. ENGELBERTS (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1292).—When PhOH is oxidised with 20% AcO_2H a 62% yield of *cis-cis*-muconic acid (I) is obtained and benzoquinone is formed. Pyrocatechol with AcO_2H gives

an excellent yield of (I). These reactions appear to afford the simplest means of transition from aromatic to aliphatic compounds. E. S. HEDGES.

Hexyl and hexenyl derivatives of phenol. C. D. HURD and R. W. McNAMEE (J. Amer. Chem. Soc., 1932, 54, 1648—1651).— Δ^{α} -Hexen- γ -ol (propylvinylcarbinol) and PCl_3 in C_6H_6 give α -chloro- Δ^{β} -hexene (I), b. p. $42\text{--}44^\circ/40$ mm., $120\text{--}122^\circ/751$ mm., the structure of which is established by reduction to *n*-hexyl chloride and hydrolysis to Δ^{β} -hexen- α -ol. α -Bromo- Δ^{β} -hexene (II), b. p. $43\text{--}45^\circ/10$ mm., $50\text{--}53^\circ/25$ mm., is prepared from the carbinol, HBr , and conc. H_2SO_4 . (I) or (II) and NaOPh in EtOH give α -phenoxy- Δ^{β} -hexene (*Ph* γ -propylallyl ether) (III), b. p. $105\text{--}107^\circ/4\text{--}5$ mm., also formed from (II) [but not (I)], PhOH , and K_2CO_3 . (I) and NaOPh in Et_2O give *o*- γ -hydroxyphenyl- Δ^{β} -hexene (*o*- γ -propylallylphenol), b. p. $144^\circ/20$ mm. Catalytic reduction of (III) gives *Ph* hexyl ether (α -phenoxyhexane), b. p. $125\text{--}128^\circ/11$ mm., m. p. -19° , also prepared from hexyl chloride and NaOPh in EtOH . γ -Bromohexane and NaOPh give γ -phenoxyhexane, b. p. $129\text{--}132^\circ/12$ mm., m. p. -35° to -33.5° ; when heated at $210\text{--}215^\circ$, (III) gives γ -*o*-hydroxyphenyl- Δ^{α} -hexene, b. p. $120\text{--}122^\circ/7$ mm. C. J. WEST (b).

Bromination of phenyl γ -chloro- Δ^{β} -propenyl ether. L. BERT and E. ANDOR (Compt. rend., 1932, 194, 1079—1081).— Br in CHCl_3 converts this ether (I) into the corresponding *p*-bromophenyl ether, b. p. $153^\circ/13$ mm. (also synthesised in 60% yield from $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{OH}$ and $\text{CHCl}_3\text{CH}_2\text{Cl}$), the HBr formed reacting with (I) to give PhOH (and hence $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{OH}$) and α -bromo- γ -chloro- Δ^{β} -propylene (this vol., 362). J. W. BAKER.

Aryl ethers of ψ -carbamide. M. BATTEGAY and H. SILBERMANN (Compt. rend., 1932, 194, 988—990).—By heating a mixture of cyanamide dihydrochloride and a phenol at a high temp. for several hr. in a stream of dry HCl , an aryl ether of ψ -carbamide is formed. *O*-*m*-Tolylcarbamide hydrochloride, m. p. $215\text{--}216^\circ$ [picrate, m. p. $243\text{--}244^\circ$ (decomp.)], is described. These aryl ethers are unstable in the free state, NH_3 resolving them into PhOH and cyanamide. Ethers of *o*- and *m*-cresol, α - and β -naphthol, and of resorcinol are prepared by the above method. J. L. D'SILVA.

Condensation of phenols with formaldehyde.
I. Formation of phenol alcohols. F. S. GRANGER (Ind. Eng. Chem., 1932, 24, 441—448).—Action of CH_2O on PhOH in presence of NaOH gives mono-, di-, and tri-hydroxymethylphenols (cf. A., 1894, i, 577). Similarly *o*-cresol with 2 mols. of CH_2O gives 4:6-dihydroxymethyl-*o*-cresol, m. p. 94° , and a small amount of (?) dihydroxydihydroxymethyl-ditolylmethane, m. p. 155° . With 1 mol. of CH_2O mono- and dialcohols are formed. *m*-Cresol gives resins and the *Na* salt of (?) 2:4:6-trihydroxymethyl-*m*-cresol. *m*-2- and -6-Xylenols give CH_2Ph_2 derivatives, the former more quickly. A similar product is obtained from ψ -cumenol. The $\text{OH}\cdot\text{CH}_2$ derivatives of *p*- and *o*-5-xylenols react slowly with a second mol. of CH_2O (cf. A., 1899, i, 34). Attempts to prepare a trihydroxymethyl derivative from *m*-5-xylenol gave resinous products. A. A. LEVI.

Mono- and di-bromo-derivatives of *m*-cresol.

R. C. HUSTON and J. A. HUTCHINSON (J. Amer. Chem. Soc., 1932, 54, 1504—1506).—*m*-Cresol and Br (1 mol.) in the cold give 4- and 6-bromo-*m*-cresol (*benzoate*, m. p. 82.5—83°; *benzenesulphonate*, m. p. 79—80°; *p*-toluenesulphonate, m. p. 84—85°), also prepared from the corresponding bromotoluidines. Dibromination gives 2 : 6- (*benzoate*, m. p. 80—81°) and 4 : 6-dibromo-*m*-cresol (*benzoate*, m. p. 84—85°).

C. J. WEST (b).

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

Benzoylation of *m*-cresol. R. C. HUSTON and A. L. HOUK (J. Amer. Chem. Soc., 1932, 54, 1506—1510; cf. A., 1931, 1047).—*m*-Cresol, $\text{CH}_2\text{Ph}\cdot\text{OH}$, and AlCl_3 in light petroleum at 35° give 4-benzyl-*m*-cresol (I), b. p. 153—155°/4 mm., m. p. 46—47° (2 : 6- Br_2 derivative, m. p. 102—103°; *benzoate*, b. p. 215—220°/5 mm., m. p. 58—59°), 6-benzyl-*m*-cresol, b. p. 168—170°/5 mm., m. p. 93—94° (2 : 4- Br_2 derivative, m. p. 86—87°; *benzoate*, m. p. 70—71°), and 4 : 6-dibenzyl-*m*-cresol, b. p. 230—232°/5 mm., m. p. 106—107° (2- Br derivative, m. p. 65—67°; *benzoate*, m. p. 88—89°). *m*-Cresol, CH_2PhCl , and Na in PhMe give (I), *m*-tolyl benzyl ether, b. p. 142—145°/5 mm., m. p. 45—46°, 2-benzyl-*m*-cresol, b. p. 157—159°/5 mm., m. p. 71—72° (benzyl ether, m. p. 71—73°; 4 : 6- Br_2 derivative, m. p. 106—107°; *benzoate*, m. p. 71—73°), and 2 : 4-dibenzyl-*m*-cresol, b. p. 216—218°/5 mm. (*benzoate*, b. p. 235—240°/5 mm.). C. J. WEST (b).

Tervalent carbon. XI. Labile radical peroxides. K. ZIEGLER and P. ORTH (Ber., 1932, 65, [B], 628—631).—The rate of absorption of O_2 by solutions of C_2Ph_6 in PhMe or CHCl_3 is considerably greater than that of dissociation of the ethane. A portion of the C_2Ph_6 is directly oxidised without previous dissociation into CPh_3 , probably owing to the formation of a particularly active, labile peroxide (cf. Haber and Willstätter, this vol., 352). Di-9-phenylfluorenyl is converted by a small excess of chloroanil in hot CHCl_3 into tetrachloroquinol di-9-phenylfluorenyl ether; the solution is indifferent to air. If a deficiency of chloroanil is used, the resulting solution very readily absorbs O_2 with formation of chloroanil. The intermediate production of a labile peroxide is postulated: $\text{R}\cdot\text{O}\cdot\text{C}_6\text{Cl}_4\cdot\text{O}\cdot\text{R} + \text{O}_2 = \text{O}\cdot\text{C}_6\text{Cl}_4\cdot\text{O} + \text{R}\cdot\text{O}\cdot\text{O}\cdot\text{R}$.

H. WREN.

Synthesis of thyroxine. A. I. BOLSCHUHN (J. Gen. Chem. Russ., 1931, 1, 1070—1074).—The condensation product of 3 : 4 : 5-tri-iodonitrobenzene with quinol Me ether (A., 1927, 358) is usually difficult to purify from accompanying tarry matter; 3 : 5-di-iodo-4-(4'-ethoxyphenoxy)nitrobenzene (I), m. p. 148—149°, is much more readily purified. Reduction of (I) with SnCl_2 in AcOH gives 3 : 5-di-iodo-4-(4'-ethoxyphenoxy)aniline hydrochloride, m. p. 220—223° in open and 224—227° in sealed capillary; the free amine has m. p. 100—101°.

G. A. R. KON.

Synthesis of derivatives of myristicin. W. BAKER, (MISS) L. V. MONTGOMERY, and H. A. SMITH (J.C.S., 1932, 1281—1283).—Methylenation of pyrogallol 1-Me ether gives 1-methoxy-2 : 3-methylenedioxybenzene, m. p. 41°, which is nitrated to give the 5- NO_2 -compound, m. p. 146—148° (lit. 143—144°); attempts

to prepare myristicin acid from the corresponding NH_2 -derivative were unsuccessful. Myristicin aldehyde is synthesised from methylene sulphate and 4 : 5-dihydroxy-3-methoxybenzaldehyde, and oxidised to the acid, each identical with the compound prepared from natural myristicin.

F. R. SHAW.

Conversion of *l*-phenylmethylcarbinol into dextro- and lævo-rotatory α -chloroethylbenzene. A. H. J. HOUSSA and H. PHILLIPS (J.C.S., 1932, 1232—1235).— COCl_2 reacts with *l*-CHPhMe·OH in the presence of either K_2CO_3 (when the *dl*-carbinol gives the chloroformate, converted into CHPhMeCl by distillation at 80—90°/13 mm.) or quinoline (1.25 mols.) to give lævorotatory CHPhMeCl, but with 3 mols. of quinoline a dextrorotatory chloride is obtained. Since, in the latter case, decomp. of the additive compound of the chloroformate and quinoline intervenes, inversion probably occurs in this case (cf. this vol., 251). *l*-CHPhMe·OH *p*-toluenesulphinate does not react smoothly with a 4% solution of HOCl at 0°, much *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ and styrene and only a little CHPhMeCl of low dextrorotation being obtained; hence it is not possible to decide whether the change in sign of rotation is due to inversion. With aq. solutions of Cl_2 or Br the *p*-toluenesulphinate yields dextrorotatory α -chloro- and α -bromo-ethylbenzene, with less by-product, whilst with ICl the *dl*-sulphinate reacts smoothly to give *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{I}$ and CHPhMeCl. The results are discussed from the viewpoint of the Walden inversion.

J. W. BAKER.

Isomerisation of phenylglycide. Affinity of the primary alcohol grouping. P. WEILL and (MLLE.) M. DARMON (Compt. rend., 1932, 194, 977—979).—Phenylglycide at 275° in a N_2 atm. affords $\text{CH}_2\text{Ph}\cdot\text{CHO}$ and products of isomerisation, from which $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$, transformed into $\text{CH}_2\text{Ph}\cdot\text{CHO}$ by heat, is isolated. The reaction indicates that the affinity of the $\text{CH}_2\cdot\text{OH}$ group is less than that of the Ph group.

J. L. D'SILVA.

Preparation of an optically active triaryl-carbinol. E. S. WALLIS (J. Amer. Chem. Soc., 1932, 54, 1695—1696).—*d*-, $[\alpha]_D^{20} +5.8^\circ$ in CCl_4 , and *l*-, $[\alpha]_D^{20} -5.4^\circ$, -phenyldiphenyl- α -naphthylcarbinols have been prepared from *l*- and *d*-phenyldiphenyl- α -naphthylthioglycolic acids, respectively. The *d*-, $[\alpha]_D^{20} +21.6^\circ$, and *l*-, $[\alpha]_D^{20} -22.7^\circ$ in Et_2O , -*Et* ethers of the carbinols are obtained from the *d*- and *l*-acids, respectively.

C. J. WEST (b).

Amino-alcohols. VIII. Benzoic esters of arylalkanolamines. W. H. HARTUNG, J. C. MUNCH, and E. B. KESTER (J. Amer. Chem. Soc., 1932, 54, 1526—1530; cf. this vol., 157).— α -Chloro- β -benzamido- α -phenylpropane, m. p. 125° (corr.), prepared by benzoylating the amine, rearranges when heated with moist Bu^nOH to β -amino- α -benzoyloxy- α -phenylpropane hydrochloride, m. p. 208° (corr.), which has a marked local anæsthetic action and about one tenth of the relative pressor action of β -amino- α -hydroxy- α -phenylpropane.

C. J. WEST (b).

Action of oxidising agents on derivatives of ergosterol. A. GUITERAS, Z. NAKAMIYA, and H. H. INHOFFEN (Annalen, 1932, 494, 116—126).—

α -Methylisovaleraldehyde (*semicarbazone*, m. p. 129—130°, $[\alpha]_D^{25}$ —52.2° in EtOH) is obtained in 13.5—31% yield by the action of 6% O_3 (in AcOH) on ergosterol (cf. Reindel and Kipphan, this vol., 267) and (a) ergosteryl- B_1 and - B_3 acetates, lumisterol, vitamin- D_2 , suprasteryl I allophanate, and suprasterol II, (b) the additive compounds from maleic anhydride and ergosterol and dehydroergosteryl acetate and from citraconic anhydride and tachysterol acetate, and (c) dihydroergosterol, showing that the side-chain double linking is not involved in (a) isomerisations by mineral acid or irradiation, (b) the conjugated system in the sterols, and (c) the addition of 2H to ergosterol. Oxidation of α -ergostenyl acetate and ergostanol with CrO_3 in AcOH gives small amounts of a liquid ketone containing 9 C atoms (probably Me γ -methylisohexyl ketone) (*semicarbazone*, m. p. 156°, $[\alpha]_D^{25}$ —16.45° in $CHCl_3$). Cholesterol, ergosterol, and sitosterol may contain the same ring systems but different side-chains. The so-called cyclopentadienetricarboxylic acid obtained by Reindel and Niederländer (A., 1930, 1578) from ergosterol and HNO_3 is probably toluene-2:3:4:5 (or 2:3:5:6)-tetracarboxylic acid (Me_4 ester, m. p. 123—124°), and is also obtained by HNO_3 -oxidation of dehydroergosterol and lumisteryl acetate (but not from vitamin- D_2 or ergosteryl- B_1 and - B_3 acetates). Contrary to Reindel and Niederländer it is not stable to oxidising agents; alkaline $KMnO_4$ converts it into benzenepentacarboxylic acid.

H. BURTON.

Benzoic esters and electronic affinities of radicals. III. A. KAKI (J.C.S., 1932, 1184—1188).—Nitration of $BzO\cdot[CH_2]_n\cdot OBz$ affords 80.8, 74.8, and 75.3% of *m*-derivative (subsequently given in parentheses) when $n=1, 2,$ and $3,$ respectively, the corresponding vals. for $BzO\cdot[CH_2]_n\cdot H$ being 72.6, 69.9, and 71.8%, and for $BzO\cdot[CH_2]_n\cdot Cl$, 81.9, 75.8, and 77.7%. Hence *m*-nitration induced by substitution in a saturated side-chain increases in the order $H < O < Cl$. The vals. obtained for cyclohexyl (67.0), 2- (65.4), 3- (67.2), and 4- (67.3)-methylcyclohexyl, compared with those for Me (72.6) and $n-C_6H_{13}$ (63.7) benzoates confirm the increased electrochemical repulsion due to increased alkyl substitution in the saturated C chain, and indicate only a slight increase (3%) in *m*-nitration due to ring closure, which cannot, therefore, be entirely responsible for the relatively large difference (20%) between benzylpiperidine (72%) and $CH_2Ph\cdot NEt_3$ (51%). The proportion of *m*-nitration observed with *p*-nitrophenyl (88%), *o*- (76%), *m*- (73%), and *p*- (75%) -nitrobenzyl benzoates indicates the order $Me > NO\cdot C_6H_4\cdot CH_2$ for directive power. The proportion of *m*-nitration of NH_2Bz (69%), benzoylpiperidine (31%), and $NBzEt_2$ (29.5%) indicates decreased *m*-substitution by substitution in the NH_2 group, but is unaffected by addition of $Be(NO_3)_2$ during nitration.

J. W. BAKER.

Salt-forming characteristics of doubly- and singly-linked elements of the oxygen group. III. Carbonyl group in ethyl benzoate. J. W. BAKER and L. HEY (J.C.S., 1932, 1226—1231).—Partition of $BzOEt$ between ligroin and H_2SO_4 and

its nitration in oleum- HNO_3 (with varying concns. of SO_3), both with and without added $(NH_4)_2SO_4$, give results exactly comparable in type with those obtained with $PhCHO$ and $PhAc$ (A., 1931, 485, 486), indicating that the same type of consecutive ionic equilibria must be present in such H_2SO_4 solution, but

hydrolysis of the oxonium salt $PhC(OEt)\cdot OH\cdot O^+SO_3H$, and repression of its ionisation by $(NH_4)_2SO_4$, are more marked than in the previous cases. The proportion of *m*-nitration (74.8%) when $BzOEt$ is nitrated in HNO_3 (d 1.53) alone is increased gradually to 93.7% when nitration is effected in the presence of H_2SO_4 containing increasing amounts (up to 5.5%) of free SO_3 , addition of $(NH_4)_2SO_4$ to the H_2SO_4 - HNO_3 medium causing a depression (8—9%) of the *m*-isomeride in each case. Addition of N_2O_5 to the HNO_3 (d 1.53) causes no appreciable increase in *m*-nitration (75.8%), indicating that, in agreement with the previous suggestion (*loc. cit.*), no true oxonium nitrate is formed.

J. W. BAKER.

Nuclei of *cis*-cinnamic acid. A. W. K. DE JONG (Rec. trav. chim., 1932, 51, 397—400).—No definite concn. of a solution of *cis*-cinnamic acid (I), m. p. 68°, in ligroin exists which will with certainty induce crystallisation in this form (cf. A., 1914, i, 173). A method is described for determining the rate of disappearance of nuclei of (I) from solution in ligroin.

R. S. CAHN.

Abietic acid. H. BERGER (J. pr. Chem., 1932, [ii], 133, 331—349).—Na abietate, when heated with $NaOH$ at 240—280°, gives amongst other products H_2 , CH_4 , CO_2 , a substance (A), tetrahydrotetene or 2:3:2'-trimethyl-4'-isopropylidiphenyl, m. p. 104°, $[\alpha]_D^{25} +106^\circ$ in MeOH, and a substance (B), $C_{17}H_{16}$ or $C_{18}H_{18}$ (possibly impure retene), m. p. 86°. (A) gives retene when heated with S, but did not yield a quinone. (B) with CrO_3 gives (?iso)butyric acid and an o-quinone (? impure retenequinone), m. p. 195° (quinoxaline derivative, m. p. 163°); (B) is unchanged by heating with S. Attempts to reduce retene catalytically and to condense 2-bromophenanthraquinone with $Pr^{\beta}Br$ failed. *o*-Nitrobenzaldehyde, K *m*-bromophenylacetate, and $ZnCl_2$ in hot Ac_2O give *o*-nitro- α -*m*-bromophenylcinnamic acid, trans-form, m. p. 238—239°, cis-form, m. p. 164°, reduced by $FeSO_4$ and aq. NH_3 to *o*-amino- α -*m*-bromophenylcinnamic acid, trans-form, m. p. 155° (decomp.), whence by diazotisation and treatment with Cu powder 2-bromophenanthrene-9-carboxylic acid was obtained; attempts to remove CO_2 from this acid failed. *oo'*-Ditolyl with S at 250° (not with Se) gives a 50% yield of phenanthrene.

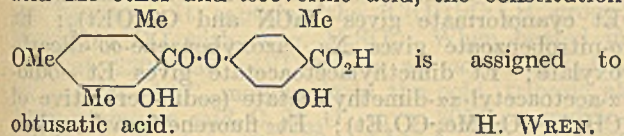
R. S. CAHN.

***l*-p-Methoxyphenylalanine.** L. D. BEHR and H. T. CLARKE (J. Amer. Chem. Soc., 1932, 54, 1630—1634).—*l*-N-Acetyltyrosine (I), a resin, $[\alpha]_{540}^{22} +46.2^\circ$ in H_2O , prepared from Ac_2O and tyrosine in hot aq. suspension (whereby about 10% racemisation occurs), separates from dioxan with 1 mol. of solvent, with m. p. 107—109° and (after cooling) 138—140°; the dioxan is removed only with difficulty. Me_2SO_4 and (I) in aq. $Ba(OH)_2$ give N-acetyl-*p*-methoxyphenylalanine, m. p. 150—151°, $[\alpha]_{540}^{25} +67.6^\circ$ in EtOH, hydrolysed by dil. mineral acids to *l*-*p*-methoxyphenyl-

alanine (II), m. p. 264—265° (corr.), $[\alpha]_{D}^{20}$ -5.9° in *N*-HCl [sulphate, m. p. 191° (corr.); hydrochloride, m. p. 237—238° (corr.); Cu salt, decomp. 250° (corr.); picrolonate, m. p. 174° (decomp., corr.); Bz derivative, m. p. 136—137°, $[\alpha]_{D}^{20}$ -3.7° in EtOH; benzene-sulphonyl derivative, m. p. 136—137°, $[\alpha]_{D}^{21}$ $+6.3^{\circ}$ in EtOH]. The phenylhydantoic acid, m. p. 176—177° (corr.), $[\alpha]_{D}^{21}$ $+123.6^{\circ}$ in EtOH, from (II) and PhNCO when boiled with 10% HCl gives the phenylhydantoin, m. p. 134—135°; the α -naphthylhydantoic acid, m. p. 167—168°, $[\alpha]_{D}^{22}$ $+63.3^{\circ}$ in EtOH, similarly affords the α -naphthylhydantoin, m. p. 155—157°.

C. J. WEST (b).

Lichen substances. XI. Constitution of obtusatic acid. Y. ASAHINA and F. FUZIKAWA (Ber., 1932, 65, [B], 580—583).—Maceration of *Ramalina calicaris* with COMe₂ followed by evaporation of the extract affords *d*-usnic acid, m. p. 200°, $[\alpha]_{D}^{18}$ $+499^{\circ}$ in CHCl₃, evernic acid, m. p. 169°, and obtusatic acid, m. p. 205° after loss of CO₂ at 195° when rapidly heated. Since *Me obtusate* *Me*₂ ether, m. p. 126—127°, is hydrolysed to rhizonic acid *Me* ether and isoevernic acid, the constitution



Lichen substances. XII. Synthesis of diffractaic acid. Y. ASAHINA and F. FUZIKAWA (Ber., 1932, 65, [B], 583—584; cf. this vol., 396).—*Me* β -orcincolcarboxylate and dimethyl- β -orcincolcarboxyl chloride in COMe₂ and *N*-NaOH afford *Me* diffractate, m. p. 127—128°, identical with the product derived from diffractaic acid and diazomethane and hydrolysed to diffractaic acid, the constitution of which (*loc. cit.*) is thereby established. H. WREN.

Cyanohydrins of type Ph·[CH₂]_{*n*}·CH(OH)·CN and Ph·[CH₂]_{*n*}·CHMe·CH(OH)·CN and the corresponding α -hydroxy-acids. (MLLE.) D. BIQUARD (Compt. rend., 1932, 194, 983—985).—The H sulphite compound (freed from aldehyde) of the appropriate aldehyde with KCN in H₂O at room temp. affords excellent yields of cyanohydrins. Hot conc. HCl hydrolyses them to the corresponding acids. Many cyanohydrins are prepared by this method. α -Hydroxy- β -phenylbutyronitrile, b. p. 133°/3 mm., and α -hydroxy- β -phenylbutyric acid, m. p. 121—122°, are described. J. L. D'SILVA.

Preparation of diarylphthalides. F. F. BLICKE and O. J. WEINKAUFF (J. Amer. Chem. Soc., 1932, 54, 1446—1453).—Mg *o*-ethoxymethylphenyl bromide (I) reacts with various methoxybenzophenones giving *tert.*-carbinols, the ·CH₂·OEt groups of which are oxidised to CO₂H with the spontaneous formation of OMe derivatives of diarylphthalides. The following substituted triphenylcarbinols are prepared from (I) or *o*-Me·C₆H₄·MgBr and the appropriate benzophenones: 2-methyl-, m. p. 100—101°; 2':4''-dimethoxy-2-methyl-, m. p. 152—154°; 4':4''-dimethoxy-2-methyl-, m. p. 109—110°; 2-ethoxymethyl-, m. p. 81—82°; 2'-methyl-2-ethoxymethyl-, m. p. 108—109°; 3'-methoxy-2-ethoxymethyl-, an oil; 4'-methoxy-2-ethoxy-

methyl-, m. p. 100—101°; 2':2''-dimethoxy-2-ethoxy-methyl-, m. p. 103—104°; 2':4''-dimethoxy-2-ethoxy-methyl-, m. p. 107—108°; 4':4''-dimethoxy-2-ethoxy-methyl-, m. p. 74—76°; 3':4''-dimethoxy-2-ethoxy-methyl-, m. p. 83—84°. 9-*o*-Tolyl- and 9-*o*-ethoxy-methylphenyl-xanthohydrols have m. p. 165—166° and 153—154°, respectively. The colorations of these compounds with H₂SO₄ are given. The following are obtained by oxidation of the requisite carbinols: diphenylphthalide; 2'-, m. p. 127—128°, 3'-, and 4'-methoxydiphenylphthalides, gums; 2':2'', m. p. 151—152°, 2':4'', m. p. 127—128°, 4':4'', m. p. 101—102°, and 3':4'', m. p. 200—201°, -dimethoxydiphenylphthalides; fluoran. 4'-Hydroxydiphenylphthalide, fluoran, isophenolphthalein, phenolphthalein, and 3':4''-dihydroxydiphenylphthalide, amorphous, are prepared by demethylation of the appropriate OMe derivatives. *iso*Phenolphthalein has no laxative effect.

2-Hydroxy-5-*o*-hydroxybenzoylbenzophenone, m. p. 131—132°, is obtained as a by-product in the prep. of 2-hydroxybenzophenone from *o*-anisoyl chloride, C₆H₅, and AlCl₃. Details are given for the prep. of 4-hydroxy- and 2:4'- and 3:4'-dihydroxy-benzophenone. Attempted prep. of isophenolphthalein from 2-*o*-hydroxybenzoylbenzoic acid (cf. Orndorff and Barrett, A., 1925, i, 35) gave phenolphthalein (40%), a little fluoran, and tar. C. J. WEST (b).

Halogen derivatives of diarylphthalides. II. F. F. BLICKE, F. D. SMITH, and J. L. POWERS (J. Amer. Chem. Soc., 1932, 54, 1465—1471; cf. A., 1929, 926).—2:6-Dichloro- and -dibromo-phenols, obtained in 80—85% yield from 3:5-dichloro- and -dibromo-4-hydroxybenzoic acids and quinoline at 190—200°, are methylated (Me₂SO₄) to 2:6-dichloro-, b. p. 105—106°/20 mm., and 2:6-dibromo-, b. p. 129—130°/20 mm., -anisoles. Condensation of 2-halogenoanisoles with phthalyl chloride (I) gives the 3:3'-dihalogenophenolphthalein *Me*₂ ethers: the dichloro-, m. p. 136—138°, dibromo- (II), and di-iodo-, m. p. 177—179° (demethylated to 3':3''-di-iodophenolphthalein, m. p. 245—246°), derivatives are prepared. 2:6-Dichloroanisole, phthalyl chloride, and AlCl₃ in CS₂ give *di*-2:6-dichlorophenyl phthalate, m. p. 142—144° (*di*-2:6-dibromophenyl ester, m. p. 216—218°), formed by demethylation of the anisole to the phenol, which then reacts with (I). 3':5':3'':5''-Tetrachloro- (*Me*₂ ether, m. p. 180—182°) and -tetrabromo-phenolphthaleins are obtained by direct halogenation of phenolphthalein. (II) is also prepared from Mg *o*-ethoxymethylphenyl bromide and 3:3'-dibromo-4:4'-dimethoxybenzophenone by oxidation of the resulting carbinol, m. p. 148°. Attempts to obtain diphenoxypthalide are described.

C. J. WEST (b).

Preparation of homophthalic acid by oxidation of indene. A. MEYER and R. VITTENET (Compt. rend., 1932, 194, 1250—1252).—Homophthalic acid, m. p. 189—190°, is prepared in a max. yield of 66% by oxidation of indene with K₂Cr₂O₇ and H₂SO₄, indanone being formed intermediately. The oxidation of chloroindane and of indanone with the same reagent follows an identical course.

H. A. PIGGOTT.

Decolorised cinnamylidenemalonic acid. A. MADINAVEITIA and J. MADINAVEITIA (Anal. Fís. Quím., 1932, 30, 120—127).—2 : 4-Diphenylcyclobutane-1 : 3-bismethylenemalonic acid (I) (Kohler, A., 1902, i, 788), obtained by insolation of cinnamylidenemalonic acid, is reduced catalytically (Pt oxide) to the *bismethylenemalonic acid* (II), m. p. 203°, which is converted by vac. distillation into the *bispropionic acid* (III), m. p. 185°. Although (III) belongs to the *trans*-series, it yields with Ac_2O an oily *anhydride* reconvertible into the acid by NaOH . Conc. H_2SO_4 causes depolymerisation of (I), but not of (II). The 4-ring in (III) is unattacked by HCl or HI . The aromatic nucleus in cinnamylidenemalonic acid can be completely hydrogenated, using Pt oxide, yielding an *acid*, $\text{C}_{12}\text{H}_{20}\text{O}_4$, m. p. 90°, and *Et* α -truxillate similarly yields an *ester*, $\text{C}_{22}\text{H}_{36}\text{O}_4$, m. p. 85°, but in α - and γ -truxillic acids, as in (I), the nuclei are unattacked.

R. K. CALLOW.

Formation and stability of β -lactones. A. KANDIAH (J.C.S., 1932, 1215—1226).—Moist Ag_2O converts bromo-acids of the type $\text{CO}_2\text{H}\cdot\text{CR}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$ in Et_2O solution into β -lactones $\text{CR}_2\left(\begin{array}{c} \text{CO} \\ \text{CH}(\text{CO}_2\text{H})\cdot\text{O} \end{array}\right)$ (I)

which are the probable intermediates in the formation of the OH-acids, the sole products obtained when Na_2CO_3 replaces Ag_2O . Distillation converts (I) into the anhydrides $\text{CR}_2\left(\begin{array}{c} \text{CO} \\ \text{CH}(\text{OH})\cdot\text{CO} \end{array}\right)$. The simulation of γ -lactonic properties in the conversion OH-acid \rightarrow β -lactone observed when $\text{R}_2=\text{Pr}^a$ (Bains and Thorpe, J.C.S., 1923, 123, 2742) is not observed when $\text{R}_2=\text{C}_5\text{H}_{10}$, even with an additional α -Me substituent. PCl_5 and Br convert 1-carboxycyclohexane-1-acetic acid into its α -Br-derivative, m. p. 142°, whence by Ag_2O in Et_2O is obtained the β -lactone, m. p. 129° (NH_2Ph salt, m. p. 116°), of α -hydroxy-1-carboxycyclohexane-1-acetic acid, m. p. 135° (*anhydride*, b. p. 170°/11 mm., m. p. 86°; *anilic acid*, m. p. 187°; *anil*, m. p. 108°), readily oxidised by cold KMnO_4 to the α -keto-acid, m. p. 132° (*quinoxaline* derivative, m. p. 249°), and finally to cyclohexane-1 : 1-dicarboxylic acid. By similar methods are obtained: α -bromo-1-carboxycyclopentane-1-acetic acid, m. p. 135°, the β -lactone, m. p. 81° (NH_2Ph salt, m. p. 118°), of the α -OH-acid, m. p. 125° (*anhydride*, m. p. 141°; *anilic acid*, m. p. 151°), oxidised to the α -keto-acid, m. p. 133°, and cyclopentane-1 : 1-dicarboxylic acid; α -bromo- β -methyl- β -ethylsuccinic acid, m. p. 126°; β -lactone, not cryst. (NH_2Ph salt, m. p. 102°), and the β -lactone, m. p. 51°, of β -methyl- β -ethyl- and $\beta\beta$ -dimethyl-malic acid. α -Bromo-2-carboxy-*trans*-hexahydrohydrindene-2-acetic acid, m. p. 136°, affords the β -lactone, m. p. 110° (NH_2Ph salt, m. p. 116°), of the α -OH-acid, m. p. 134°, and the *cis*-acid, m. p. 164°, affords the β -lactone, m. p. 125° (NH_2Ph salt, m. p. 135°), of the α -OH-acid, m. p. 192°. Condensation of cyclohexanone cyanohydrin with $\text{CN}\cdot\text{CHNa}\cdot\text{CO}_2\text{Et}$ and subsequent methylation affords *Et* 1-cyanocyclohexane-1- α -cyanopropionate, m. p. 51°, hydrolysed to 1-carboxycyclohexane-1- α -propionic acid, m. p. 110° (*anhydride*, m. p. 165°/10 mm.; *anilic acid*, m. p. 165°; *anil*, m. p. 100°), brominated in ultra-violet light to the α -Br-acid, m. p. 142° (*bromoanhydride*, m. p. 55°), whence the β -lactone,

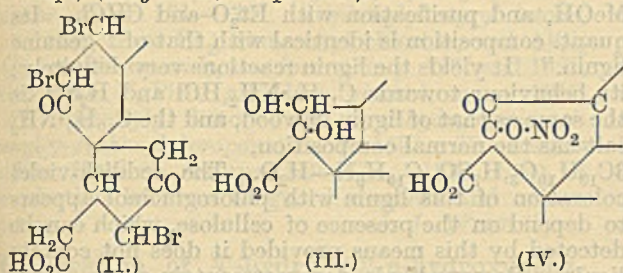
m. p. 46°, of the α -OH-acid, m. p. 73·4°, is obtained. Bromotrimethylsuccinic acid, m. p. 185°, similarly gives the β -lactone. Malonic acid and COPr^a_2 with Ac_2O and H_2SO_4 give α -carboxy- β -hydroxy- β -n-propylhexolactone, $\text{CO}_2\text{H}\cdot\text{CH}\left(\begin{array}{c} \text{CPr}^a_2 \\ \text{CO} \end{array}\right)\cdot\text{O}$, m. p. 89°, 1-hydroxycyclopentane-, m. p. 73°, and 1-hydroxycyclohexane-, m. p. 95°, -1-malonolactone being similarly obtained from cyclopentanone and -hexanone.

J. W. BAKER.

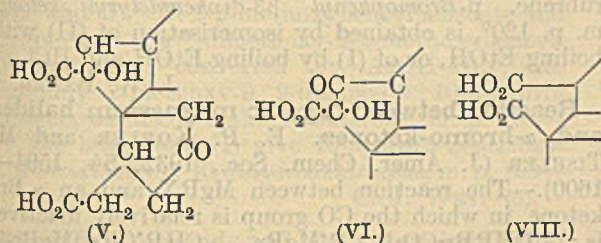
Addition of alkali enolates to esters. VI. F. ADICKES, W. BRUNNERT, O. LÜCKER, and G. SCHÄFER (J. pr. Chem., 1932, [ii], 133, 305—330; cf. A., 1931, 196).— BzOEt , *Et* *o*- and *p*-chlorobenzoate, trimethylacetate (best prepared by esterification by HCl and MeOH), triphenylacetate, benzylfluorene-9-carboxylate, benzenesulphonate, Et_4 methanetetracarboxylate, Et_3 chloromethanetricarboxylate and trimesate, Et_6 ethanehexacarboxylate, Et_2 dibenzyl- and diphenoxy-malonate, cyclopropane-1 : 1-dicarboxylate, and fluorenylsuccinate do not react with NaOEt in dry Et_2O . The following do not form additive compounds but react as stated: *Et* cyanofornate gives NaCN and $\text{CO}(\text{OEt})_2$; *Et* *o*-nitrobenzoate gives Na_2 azoxybenzene-*oo'*-dicarboxylate; *Et* dimethylacetoacetate gives *Et* sodio- α -acetoacetyl- $\alpha\alpha$ -dimethylacetate (sodio-derivative of $\text{CH}_2\text{Ac}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$); *Et* fluorene-9-carboxylate gives the sodio-derivative, $\text{C}_{12}\text{H}_8\cdot\text{CNa}\cdot\text{CO}_2\text{Et}, \text{EtOH}$; *Et* triethoxyacetate, Et_2 diethoxy- and dichloromalonate, Et_2 fluorene-9 : 9-dicarboxylate (from ClCO_2Et and *Et* fluorene-9-carboxylate in pyridine, or with NaOEt in dry Et_2O) (m. p. 99·5° after sintering at 88·5°, b. p. 220—222°/13 mm., monoclinic, β 114° 36', $a : b : c$ 0·8224 : 1 : 0·8346), and Et_4 oxalomethanetricarboxylate decompose; Et_2 benzylidene-malonate and fumarate add NaOEt at the ethylenic linking; *Et* cinnamate reacts very slowly. *Et* phenylglyoxylate and trimethylpyruvate, Et_3 phthalonate and ketomalonate add 1 mol. of NaOEt either at the CO_2Et or CO group. Parallelism exists between the ability of an ester to add NaOEt and of the corresponding ketone to form a hydrate, but no parallelism with the dissociation const. of the acid. The additive compound of *Et* trifluoroacetate and NaOEt is not colloidal, since it passes through a "Cella" filter. R. S. CAHN.

Constitution of the bile acids. XXXVII. Degradation of ring III. XXXVIII. Oxidation of 3 : 7-dihydroxycolenic acid. Structure of ring III. H. WIELAND and E. DANE (Z. physiol. Chem., 1932, 206, 225—242, 243—254; cf. A., 1931, 957).—XXXVII. Bromination of the diketodicarboxylic acid, $\text{C}_{23}\text{H}_{34}\text{O}_8$ (I), in AcOH yields a tribromodiketodicarboxylic acid, $\text{C}_{23}\text{H}_{31}\text{O}_8\text{Br}_3$ (II), m. p. 203—207° (decomp.), reduced by Zn dust and HCl in AcOH to (I). Aq. $\text{Ba}(\text{OH})_2$ converts (II) into a bromodihydroxyketotricarboxylic acid, $\text{C}_{23}\text{H}_{33}\text{O}_9\text{Br}$ (III), m. p. 250—252° (decomp.) (*Me* ester, m. p. 135°), probably by autoxidation of the primarily formed diketone to the hydroxydiketone, which then undergoes a benzilic acid transformation. (III) liberates about 60% of the theoretical amount of CO with conc. H_2SO_4 . Oxidation of (III) with fuming HNO_3 gives

a nitrate, $C_{23}H_{30}O_{11}NBr$ (IV), m. p. 215—223° (decomp.) (Me_3 ester, m. p. 168°).



Oxidation of (III) with CrO_3 in $AcOH$ yields a *lactonic acid*, $C_{22}H_{30}O_9$, m. p. 210—213° (isomeric *lactone*, m. p. 253—256°; Me ester, m. p. 115°). Reduction of (III) with Zn dust or catalytically gives the *acid*, $C_{23}H_{34}O_9$ (V), m. p. 238—240° (Me_3 ester, m. p. 131°, contains two OH groups, gives an *Ac* derivative, m. p. 122°), also obtained by the action of Zn dust and $AcOH$ on (IV). Oxidation of (V) with $Pb(OAc)_4$ or CrO_3 gives an *acid*, $C_{23}H_{22}O_9$ (VI), m. p. 226—228°, $[\alpha]_D -11.9^\circ$, titrating as tribasic in the cold, tetrabasic on heating. It contains the $C(OH)\cdot CO_2H$ group, liberating CO with conc. H_2SO_4 . When heated in vac. at 220—230°, (VI) yields an *acid*, $C_{23}H_{30}O_8$, m. p. 190—195°, monobasic in the cold, tribasic at 100°, giving an *acid*, $C_{22}H_{32}O_7$, m. p. 205°, on acidification of the hot titrated solution. Oxidation of (V) with fuming HNO_3 affords biloidanic acid (VII), with CrO_3 in $AcOH$, a *ketotetracarboxylic acid* (VIII), $C_{25}H_{32}O_9$, m. p. 153° (+ H_2O of cryst.) $[\alpha]_D +62.0^\circ$ (Me_4 ester, m. p. 103°). $KOBr$ oxidises (VIII) to (VII). In high vac. at 330—335°, (VIII) gives a *product*, $C_{21}H_{30}O_6$, m. p. 170—175°. (VIII) is also obtained by CrO_3 oxidation of norcilianic acid. $KOBr$ oxidises (VI) and (V) to a *pentabasic acid*, m. p. 250—252°. The lactone ring is not opened on hot titration.



Oxidation of (III) with $Pb(OAc)_4$ gives an *acid* (IX), $C_{23}H_{31}O_9Br$, m. p. 183—185° (decomp.), from which the Br is eliminated on titration. On treatment with Zn dust and $AcOH$, the Br is replaced by H , yielding (VI). Oxidation of (IX) with CrO_3 gives (VIII).

XXXVIII. Oxidation of 3:7-dihydroxycholenic acid (I) with alkaline $KMnO_4$ affords *tetrahydroxycholenic acid* (II), $C_{24}H_{40}O_6$, m. p. 223—225°, which is further oxidised by fuming HNO_3 forming the *nitrate* (III), m. p. 223° (decomp.), of (IV) (below). Reduction of (III) in $AcOH$ with Zn dust and HCl or with hyposulphite gives *dihydroxyisodeoxybilianic acid* (IV), m. p. 290° (decomp.) (Me_3 ester, m. p. 187°), which, when boiled with HCO_2H , gives a doubly unsaturated *acid*, $C_{24}H_{32}O_7$, m. p. about

192°, and with HI and red P in $AcOH$ gives *monohydroxyisodeoxybilianic acid*, m. p. 280—285° (decomp.). Thermal decomp. of (IV) yields a *pyro-acid*, $C_{23}H_{30}O_4$. Oxidation of (II) with $Pb(OAc)_4$ gives a small amount of an *acid*, $C_{24}H_{38}O_6$, m. p. 200—202° (decomp.). Oxidation of (I) with BzO_2H in $CHCl_3$ yields *dihydroxycholenic acid oxide*, m. p. 181—182° (intense orange-brown colour with $Ac_2O-H_2SO_4$), which with H_2O at 115° affords *dihydroxycholadienic acid*, m. p. 242—244°, giving apocholeic acid on catalytic hydrogenation. The group $:CHMe$ in ring III is thus probably between C_1 and C_9 but may be between C_{11} and C_{12} . J. H. BIRKINSHAW.

Photobiological properties of bile acids. I. Formation of β -cholic acid from cholic acid by ultra-violet irradiation. Z. URAKI (Z. physiol. Chem., 1932, 207, 16—24).— Me α -cholate (ordinary Me cholate) on ultra-violet irradiation in $CHCl_3$ yields an isomeric Me β -cholate, m. p. 162°, $[\alpha]_D^{25} +25.0^\circ$ in $CHCl_3$, giving a very slow Mylius reaction and regenerating α -cholic acid on hydrolysis. A *resin*, $[\alpha]_D^{25} +26.6^\circ$ in $MeOH$, probably a polymeride, yielding on hydrolysis an *acid*, $[\alpha]_D^{25} +25.0^\circ$, is also produced. Irradiation of cholic acid in $EtOH$ produced a change in rotation, but no β -cholic acid was found. With Na cholate and Et deoxycholate there was no change. Both Me α - and β -cholates give the same Me dehydrocholate on oxidation with CrO_3 . The change from α - to β -form probably involves steric inversion at the OH group in ring III. J. H. BIRKINSHAW.

Autoxidation of some benzaldehyde derivatives. P. A. A. VAN DER BEEK (Rec. trav. chim., 1932, 51, 411—413).—*p*-Bromo- (I), *o*-, *m*-, and *p*-chloro-benzaldehyde in Ac_2O absorb 1 mol. of O_2 in 1—2 weeks to form peroxides almost quantitatively. (I) gives a *substance*, m. p. 66.6°, probably $C_6H_4Br\cdot CO\cdot O_2\cdot Ac$. In $COMe_2$ only 1 atom of O is absorbed and little peracid is formed. R. S. CAHN.

Characteristics of vanillin and coumarin. R. M. HITCHENS (Ind. Eng. Chem., 1932, 24, 418—419).—A measurement of solubilities of vanillin and coumarin in $EtOH-H_2O$ and in glycerol- H_2O mixtures. A. A. LEVI.

Nitration of *O*-benzylvanillin. P. V. NAIR and R. ROBINSON (J.C.S., 1932, 1236—1239).—Nitration of *O*-benzylvanillin with HNO_3 (*d* 1.46) at 0° affords a mixture of *O*-*o*- (I), m. p. 174—176° (*phenylhydrazone*, m. p. 190—192°; *oxime*, m. p. 142—144°; *phenylimine*, m. p. 138—140°), and *O*-*p*- (II), m. p. 212—214° (main product) (*phenylhydrazone*, m. p. 208°; *oxime*, m. p. 158—160°; *phenylimine*, m. p. 192—193°), *nitrobenzyl-6-nitrovanillin*, also obtained by similar nitration of *O*-*o*-, m. p. 128—130°, and *O*-*p*-, m. p. 124°, *nitrobenzylvanillin* (obtained by heating vanillin, the $NO_2\cdot C_6H_4\cdot CH_2Cl$, and K_2CO_3 in $COMe_2$), respectively. Oxidation of (I) or (II) with $KMnO_4$ gives, respectively, *O*-*o*-, m. p. 201—202°, and *O*-*p*-, m. p. 208°, *nitrobenzyl-6-nitrovanillic acid*, converted by boiling HNO_3 (*d* 1.42) into *O*-*p*-*nitrobenzyl-4:5-dinitroguaiacol*, m. p. 178—180°, hydrolysis and methylation of which gives 4:5-dinitroveratrole. Hydrolysis of (II) with conc. H_2SO_4 at 50—60° affords 6-*nitrovanillin*, m. p. 207° (*phenylhydrazone*, m. p. 198°). J. W. BAKER.

Arylviny- and aralkylvinyl-carbinols; conversion into β -homoacraldehydes. R. DELABY (Compt. rend., 1932, 194, 1248—1250).—The following are prepared by interaction of acraldehyde with the appropriate Grignard reagent: vinylphenyl-, b. p. $77^{\circ}/2$ mm.; *o*-tolyl-, b. p. 92 — $93^{\circ}/2$ mm.; *p*-tolyl-, b. p. $90^{\circ}/2$ mm.; benzyl-, b. p. 111 — $113^{\circ}/12.5$ mm.; β -phenylethyl-, b. p. $105^{\circ}/3$ mm., and γ -phenylpropylvinylcarbinol, b. p. $112^{\circ}/2$ mm. They are converted by HBr or PBr₃ into bromides of the type CHR:CH·CH₂Br, viz., cinnamyl bromide, b. p. 111 — $114^{\circ}/4$ mm.; β -*o*-tolyl-, b. p. 115 — $116^{\circ}/2$ mm.; β -*p*-tolyl-; β -benzyl-, b. p. 126 — $130^{\circ}/10.5$ mm.; β -(β' -phenylethyl)-, b. p. $117^{\circ}/1$ mm., and β -(γ' -phenylpropyl)-allyl bromide, b. p. 117 — $120^{\circ}/0.7$ mm. Condensation of these with hexamethylenetetramine, and hydrolysis of the resulting quaternary bromides (cf. A., 1913, i, 1395) gives the corresponding aldehydes, e.g., β -*o*-tolyl-, b. p. 139 — $141^{\circ}/16$ mm., β -*p*-tolyl-, b. p. 145 — $146^{\circ}/16$ mm., β -(β' -phenylethyl)-, b. p. 115 — $117^{\circ}/2$ mm. (semicarbazone, m. p. 195.5°), and β -(γ' -phenylpropyl)-acraldehyde, b. p. 126 — $128^{\circ}/2.5$ mm. (semicarbazone, m. p. 172.7°). H. A. PIGGOTT.

Lignosulphonic acids. P. KLASON (Svensk Kem. Tidskr., 1932, 44, 85—89).—A discussion of the chemical constitution of the α - and β -acids.

H. F. HARWOOD.

Lignin. VI. Distillation of alkali-lignin with zinc dust in an atmosphere of hydrogen. M. PHILLIPS and M. J. GOSS (J. Amer. Chem. Soc., 1932, 54, 1518—1521; cf. A., 1931, 469).—Alkali-lignin, isolated from maize cobs, heated with Zn dust in H₂ at a max. temp. of 400° , gives an oily distillate separable into phenolic and "neutral" fractions. Guaiacol and 4-propylguaiacol are isolated from the former, whilst oxidation of the latter fraction with KMnO₄ affords anisic acid. The results indicate that the lignin mol. contains at least two aromatic nuclei or groups readily convertible into aromatic nuclei.

C. J. WEST (b).

Lignin of Coniferae. XVI. P. KLASON (Ber., 1932, 65, [B], 625—628; cf. this vol., 57).—Drastic treatment accomplishes the complete methylation of α -ligninsulphonic acid and partly affects the phenolic OH. The double linkings of the acid can be methylated, doubtless in consequence of primary addition of H₂O. Oxidation of the trimeric acid with H₂O₂ in presence of FeCl₃ gives a partly demethoxylated carboxylic acid pptd. as the naphthylamine salt, 2C₁₀H₁₀O₃·C₉H₈O₃·O·H₂SO₃·C₁₀H₉N, or, after neutralisation with alkali, as the salt

2C₁₀H₁₀O₃·C₉H₈O₃·O·H₂SO₃·2C₁₀H₉N. β -Lignin-sulphonic acid is hydrolysed by H₂SO₃ at 130° ; the product yields the mixed naphthylamine salts, 2C₉H₉O₄·H₂SO₃·C₁₀H₉N—H₂O and C₁₀H₁₀O₃·H₂SO₃·C₁₀H₉N—H₂O. Methylation of the β -acid removes its tendency to polymerise; the methylated acid is indifferent to H₂O₂, is not pptd. by C₁₀H₇·NH₂ or hydrolysed by H₂SO₃. Methylation of melaligninsulphonic acid followed by dialysis and pptn. with β -C₁₀H₇·NH₂ gives a salt, 2C₉H₁₀O₄·C₁₀H₁₀O₃·H₂SO₃·C₁₀H₉N—H₂O, the "aldol H₂O" being methylated but not the two phenolic OH groups. Free, alcohol-sol., reserve lignin is isolated

by treating the finely-divided wood with Et₂O to remove fat and resin, extraction of the residue with MeOH, and purification with Et₂O and CHCl₃. Its quant. composition is identical with that of "genuine lignin." It yields the lignin reactions very definitely; its behaviour towards C₁₀H₇·NH₂, HCl and H₂SO₃ is the same as that of lignin in wood, and the C₁₀H₇·NH₂ salt has the normal composition, 3C₁₀H₁₀O₃·H₂SO₃·C₁₀H₉N—H₂O. The reddish-violet coloration of this lignin with phloroglucinol appears to depend on the presence of cellulose, which can be detected by this means provided it does not contain lignin. Reserve lignin does not contain sugar. It is formed independently between the annual rings where high pressure exists. The hemicellulose is not combined with the lignin. H. WREN.

Phosphorus-chlorine derivatives of dibenzoylmethane. R. BURET (Compt. rend., 1932, 194, 1353—1356).—Interaction of CH₂Bz₂ and PCl₅ gives different products according to the solvent used; these could not be purified, but gave pure CH₂Bz₂, HCl, and H₃PO₄ with H₂O, and were also decomposed by EtOH. In Et₂O and C₆H₆, respectively, the compounds C₁₅H₁₁O₂PCl₄, m. p. 115 — 116° , and C₁₅H₁₂O₂·POCl₃, m. p. 137 — 138° , and in CHCl₃ a substance, m. p. 180° , are formed.

H. A. PIGGOTT.

Acetylenic arylcarbinols. Diphenyl-*p*-bromophenylacetylenylcarbinol and its derivatives: conversion into the ethylenic ketone. N. DRISCH (Compt. rend., 1932, 194, 1170—1172).—MgPhBr and *p*-C₆H₄Br·C:CH afford diphenyl-*p*-bromophenylacetylenylcarbinol (I), m. p. 99 — 100° (60% yield), converted by cold conc. H₂SO₄ and ROH into its Me, m. p. 144 — 145° , and Et, m. p. 108 — 109° , ether, and by PCl₃ into α -chloro- α -diphenyl- γ -(*p*-bromophenyl)- Δ^{β} -propinene (II), m. p. 108 — 109° (decomp.), slow heating causing decomp. at 95° into a dibromorubrene. *p*-Bromophenyl $\beta\beta$ -diphenylstyryl ketone, m. p. 120° , is obtained by isomerisation of (II) with boiling EtOH, or of (I) by boiling EtOH and HCl.

J. W. BAKER.

Reaction between organic magnesium halides and α -bromo-ketones. E. P. KOHLER and M. TISHLER (J. Amer. Chem. Soc., 1932, 54, 1594—1600).—The reaction between MgRX and an α -Br-ketone, in which the CO group is relatively inactive, is: CHR:CO·R + R'MgBr \rightarrow CHR:CR·OMgBr + R'Br. Thus, MgMeI and Ph α -bromo- $\alpha\beta\beta$ -triphenylethyl ketone give (after decomp. with dil. acid) Ph $\alpha\beta\beta$ -triphenylethyl ketone; with MgPhBr, the enolate CHPh₂·CPh:CPh·OMgBr (the free enol absorbs O₂ from the air forming a peroxide) results. MgPhBr and Ph α -iodo- $\beta\beta$ -diphenylethyl ketone, m. p. 184 — 185° (decomp.), give PhI and CHPh₂·CH:CPh·OMgBr, converted by CO₂ into α -benzoyl- $\beta\beta$ -diphenylpropionic acid (Et ester, m. p. 135 — 136° , also prepared from CH₂Bz·CO₂Et, CHPh₂Br, and NaOEt) and by BzCl into $\alpha\alpha$ -dibenzoyl- $\beta\beta$ -diphenylethane.

C. J. WEST (b).

Reaction between keto-oxido-compounds and Grignard reagents. E. BERGMANN and H. A. WOLFF (J. Amer. Chem. Soc., 1932, 54, 1644—1647).—Anisyl styryl ketone and alkaline H₂O₂ in MeOH give

α-anisoyl-*β*-phenylethylene oxide, m. p. 75°, converted by MgPhBr into *α*-*β*-dihydroxy-*αβγ*-triphenyl-*γ*-anisylpropane, m. p. 131—132°. Diphenyl styryl ketone, m. p. 165°, from Ph₂ cinnamoyl chloride, and AlCl₃ in CS₂, yields an oxide, two forms, m. p. 126° and 162°, which with MgPhBr affords a *pinacol*, m. p. 181°, of Ph diphenyl ketone, and *α*-*β*-dihydroxy-*ααγ*-triphenyl-*γ*-diphenylpropane, m. p. 159°. The results confirm Kohler's interpretation (A., 1931, 354) of the reaction between Grignard reagents and oxidoketones.
C. J. WEST (b).

Preparation of 4'-hydroxy-2-*p*-hydroxybenzoylbenzophenone. F. F. BLICKE and O. J. WEINKAUFF (J. Amer. Chem. Soc., 1932, 54, 1454—1459).—The Me₂ ether (I), m. p. 157—159° [*dioxime*, m. p. 177—178° (decomp.); *diphenylhydrazone*, m. p. 171—173°], of 4'-hydroxy-2-*p*-hydroxybenzoylbenzophenone (II), m. p. 225—226°, is prepared from (a) *o*-C₆H₄(CO)₂O and *p*-OMe·C₆H₄·MgI, (b) Me 2-anisoylbenzoate and *p*-OMe·C₆H₄·MgI, (c) phenolphthalein, and (d) 4 : 4'-dimethoxytriphenylmethane-2-carboxylic acid (converted by conc. H₂SO₄ into 2 : 5-dianisyl-3 : 4-benzofuran, m. p. 126—127°); (I) is demethylated to (II). (I) and N₂H₄·H₂O in AcOH give 3 : 6-dianisyl-4 : 5-benzopyridazine, m. p. 205—206°. The compound described (lit.) as "dihydroxyphenylanthranol" is (II).
C. J. WEST (b).

Preparation of substituted anthrones. F. F. BLICKE and O. J. WEINKAUFF (J. Amer. Chem. Soc., 1932, 54, 1460—1464).—Anthraquinone and *p*-OMe·C₆H₄·MgI (I) give 9-hydroxy-9-*p*-anisyl-10-anthrone, m. p. 206—207°. 2-*p*-Methoxybenzylbenzoic acid and conc. H₂SO₄ give 2-methoxy-9-anthrone, m. p. 94—95° (structure proved by oxidation), which with (I) affords 2-methoxy-9-anisylanthracene, m. p. 175—176°, oxidised by Na₂Cr₂O₇ in AcOH to 9-hydroxy-2-methoxy-9-anisyl-10-anthrone, m. p. 199—201°, also formed from 2-methoxyanthraquinone and (I). Et 2-*p*-methoxybenzylbenzoate and (I) give 4'' : 4'''-dimethoxy-2-*p*-methoxybenzyltriphenylcarbinol, converted by AcOH-HCl into the gummy 2-methoxy-9 : 9-dianisyl-9 : 10-dihydroanthracene, oxidised to the 10-anthrone, m. p. 182—183°; the latter and (I) give 10-hydroxy-2-methoxy-9 : 9 : 10-trianisyl-9 : 10-dihydroanthracene, m. p. 193—194°.
C. J. WEST (b).

Benzoylbenzoic acids and their transformation into anthraquinones. A. OLIVERIO (Gazzetta, 1932, 62, 231—243).—A crit. examination of previous work.
E. E. J. MARLER.

Synthesis of munjistin. P. C. MITTER and H. BISWAS (Ber., 1932, 65, [B], 622—625).—2-Chloro-6-methoxytoluene is converted by phthalic anhydride in presence of CS₂ and AlCl₃ into *o*-2'-chloro-4'-methoxy-3'-methylbenzoylbenzoic acid, m. p. 202°, transformed by H₂SO₄ into 4-chloro-2-methoxy-3-methylanthraquinone (I), m. p. 197°. (I) and AlCl₃ at 200° afford 4-chloro-2-hydroxy-3-methylanthraquinone, m. p. 324—325°, oxidised by treatment with H₂SO₄ and H₃BO₃ and then with NaNO₂ to a substance, m. p. 231°, which does not depress the m. p. of natural munjistin (1 : 3-dihydroxyanthraquinone-2-carboxylic acid), but is not free from Cl. (I) and SO₂Cl₂ in

presence of PhNO₂ transform 3-methylalizarin into 4-chloro-3-methyl-1 : 2-dihydroxyanthraquinone, m. p. 178—180°, oxidised at 160—165° to purpurin, but yielding at 145—150° a compound with the same m. p. as 1 : 2 : 4-trihydroxyanthraquinone-3-carboxylic acid, but not free from Cl. Repeated reduction of this compound with Na₂S₂O₄ and NH₃ followed by treatment with boiling aq. Ba(OH)₂ yields an insol. Ba salt from which a Cl-free product, m. p. 229—230°, is obtained which does not depress the m. p. of natural munjistin.
H. WREN.

Tautomerism of anthraquinone-1 : 5-dicarboxyl chloride and synthesis of members of the hetero-coerdianthrene series. Stereochemistry of difficultly hydrolysable esters. R. SCHOLL, H. K. MEYER, and W. WINKLER (Annalen, 1932, 494, 201—224).—The Friedel-Crafts reaction with anthraquinone-1 : 5-dicarboxyl chloride (I) and ArH resembles that with anthraquinone-1-carboxyl chloride (this vol., 274), and gives mixtures of 1 : 5-diaroylanthraquinones and 9 : 10-dihydroxy-9 : 10-diaryl-9 : 10-dihydroanthracene-1 : 5-dicarboxylic acid dilactones. The former is usually the main product when a little FeCl₃ is the catalyst (at high temp.) in absence or presence of PhNO₂, whilst the latter predominates with a stoichiometrical proportion of AlCl₃ in PhNO₂ usually at 0—20°. Interconversion (under the conditions of their formation) of these products has not been accomplished.

[With S. HASS.] (I) and a little FeCl₃ in boiling *m*-xylene give 65% of 1 : 5-di-2' : 4'-dimethylbenzoylanthraquinone, m. p. 263° (*bis*-*o*-diazine, m. p. 330°). With AlCl₃ in PhNO₂ at 0—20°, the main product is the dilactone, m. p. 328.5—329°, of 9 : 10-dihydroxy-9 : 10-*m*-4'-xylyl-9 : 10-dihydroanthracene-1 : 5-dicarboxylic acid; a little 1-2' : 4'-dimethylbenzoylanthraquinone-5-carboxylic acid, m. p. 288—289° (decomp.), is also produced.

[With H. VON HOESSLE.] 1 : 5-Di-2' : 5'-dimethylbenzoylanthraquinone, m. p. 273—274°, and the dilactone, m. p. 327—328° (slight decomp.), of 9 : 10-dihydroxy-9 : 10-*di*-*p*-xylyl-9 : 10-dihydroanthracene-1 : 5-dicarboxylic acid are similarly prepared from (I) and *p*-xylene.

(I) and C₆H₆ give 1 : 5-dibenzoylanthraquinone, m. p. 277—279°, sublimes at 300—350°/20 mm., and the dilactone, m. p. above 360°, of 9 : 10-dihydroxy-9 : 10-diphenyl-9 : 10-dihydroanthracene-1 : 5-dicarboxylic acid (II). This dilactone is reduced by red P and HI (*d* 1.7) in AcOH to 9 : 10-diphenylanthracene-1 : 5-dicarboxylic acid (III) (*Et* ester, m. p. 233—234°, prepared by the Ag salt method), whilst (II) is reduced by Zn dust, aq. NH₃, and a little CuSO₄ to 9 : 10-diphenyl-9 : 10-dihydroanthracene-1 : 5-dicarboxylic acid (IV) (*Et* ester, m. p. 186—188°), also formed from (III), Zn dust, and 10% NaOH at 200°. (III) and conc. H₂SO₄ at 50—60° give a green solution of hetero-coerdianthrene (7' : 7'') (V), bronze with violet reflex [the unknown parent hydrocarbon (V, where :O=H₂) is designated hetero-coerdianthrene], also formed when (IV) is heated at about 350° or treated with conc. H₂SO₄ at 80°, from (III) and Ac₂O containing a trace of mineral acid, and by treatment of the dilactone of (II) with Al powder and conc.

H_2SO_4 . (V) undergoes oxidation in various solvents in sunlight to the 9:10-dihydroxy-9:10-dihydro-derivative, colourless, which is readily reduced (even when warmed with org. solvents) to (V). Reduction of (V) with red P and HI (*d* 1.7) at 200° and treatment of the reaction product with Zn and pumice gives 1:2:7:8-dibenzperylene in very small yield. Reduction of (V) with alkaline $\text{Na}_2\text{S}_2\text{O}_4$ and treatment of the blue vat with $\text{Et}_2\text{O}-p\text{-C}_6\text{H}_4\text{Br}\cdot\text{COCl}$ afford 3:9-di-*p*-bromobenzoyloxy-1:2:7:8-dibenzperylene. The following are also prepared: 9:10-dihydroxy-9:10-di-*p*-tolyl-9:10-dihydroanthracene-1:5-dicarboxylic acid dilactone; 1:5-di-*p*-chlorobenzoylanthraquinone, m. p. 333—334°; 9:10-dihydroxy-9:10-di-*p*-chlorophenyl-9:10-dihydroanthracene-1:5-dicarboxylic acid (dilactone, not melted at 360°), converted by conc. H_2SO_4 and Al powder at 25° into 5':5''-dichloro-hetero-coerdianthrone, violet.

[With C. SEER and O. DISCHENDORFER.] 9:10-Dihydroxy-9:10-di- α -naphthyl-9:10-dihydroanthracene-1:5-dicarboxylic acid dilactone, not melted at 360°, obtained with (probably) 1:2:7:8-dinaphthoperylene-3:9-quinone from (I), C_{10}H_8 , and AlCl_3 in PhNO_2 at 0°, when heated with soda-lime at 350° gives C_{10}H_8 and anthraquinone.

[With A. KELLER.] 4:8-Dichloroanthraquinone-1:5-dicarboxyl chloride, C_8H_6 , and AlCl_3 in PhNO_2 at 0—20° give almost entirely 4:8-dichloro-9:10-dihydroxy-9:10-diphenyl-9:10-dihydroanthracene-1:5-dicarboxylic acid dilactone; this dissolves in conc. H_2SO_4 to a colourless solution which when treated with Cu at 100° gradually becomes green owing to coerdianthrone formation.

[With G. LANGBEIN.] 2:4:6:8-Tetrabromo-1:5-diaminoanthraquinone, m. p. about 340° (from the diamino-compound and Br in H_2O), is converted by the usual method into 2:4:6:8-tetrabromoanthraquinone-1:5-dicarboxylic acid, darkens about 310° (*Et* ester).

[With H. DEHNERT.] 1:5-Dicyano-2:6-dimethylanthraquinone, darkens at 350°, not melted at 420°, is hydrolysed by H_2SO_4 at 170—175° to 2:6-dimethylanthraquinone-1:5-dicarboxylic acid, decomp. about 350° (previous darkening); the chloride and FeCl_3 in boiling C_6H_6 give mainly 9:10-dihydroxy-9:10-diphenyl-2:6-dimethyl-9:10-dihydroanthracene-1:5-dicarboxylic acid dilactone, m. p. 382—383° (previous darkening).

Et 9:10-diphenylanthracene-1:5-dicarboxylate (above) is hydrolysed only to the extent of 10% by 25% $\text{MeOH}-\text{KOH}$ after 30 hr.; this difficulty of hydrolysis is ascribed to diplanar configuration of the ester mol., the CO groups being screened by Ph.

H. BURTON.

Podophyllin. W. BORSCHÉ and J. NIEMANN (Annalen, 1932, 494, 126—142).—Podophyllotoxin (I), extracted from *Podophyllum indicum*, is $\text{C}_{22}\text{H}_{22}\text{O}_8$ (cf. Dunstan and Henry, J.C.S., 1898, 73, 209), m. p. (anhyd.) 114—118° (+ H_2O , 0.5*EtOH*) 106—108° (decomp.) (+0.5 H_2O , 0.5 COMe_2) 114—117 (decomp.) (+ H_2O , 0.5 C_6H_6) 112—115° (de-

comp.), $[\alpha]_D^{25} -101.3^\circ$ in EtOH , contains 3 OMe and 2 OH groups (Zerevitinov), and gives (with Ac_2O alone) an *Ac* derivative, m. p. 179—181°, $[\alpha]_D^{25} -134.9^\circ$ in CHCl_3 . (I) is isomerised by 2*N*- Na_2CO_3 in MeOH , 10% NaOAc in EtOH , and during attempted reduction (colloidal Pd, H_2 , MeOH) to picropodophyllin (II) (+ MeOH and EtOH), m. p. 227°, $[\alpha]_D^{25} +5.32^\circ$ in CHCl_3 , also containing 3 OMe and 2 OH groups and acetylated ($\text{Ac}_2\text{O}-\text{NaOAc}$) to an *Ac* derivative (III), m. p. 215—216°, $[\alpha]_D^{25} +17.7^\circ$ in CHCl_3 , also formed by similar acetylation of (I). (I) and (II) are unaffected by diazomethane (*i.e.*, no phenolic OH groups), do not contain $\cdot\text{CHO}$ or $\cdot\text{CO}$, and are converted by *N*- NaOH into podophyllin acid, $\text{C}_{22}\text{H}_{24}\text{O}_9$ (+3 H_2O) (IV), m. p. 163—165° (decomp.), $[\alpha]_D^{25} -102.8^\circ$ in EtOH (*Na* salt), also formed similarly from (III). When (IV) is heated alone or in H_2O or EtOH , (II) results. (III) and conc. H_2SO_4 in Ac_2O give apocropodophyllin, $\text{C}_{22}\text{H}_{20}\text{O}_7$, m. p. 214—216°, $\alpha=0^\circ$ [also formed from (II) and $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$ or PCl_5 in CHCl_3 , but not by thermal decomp. of (I) or (II)], reduced (H_2 , Pt-black, AcOH) to deoxypicropodophyllin, $\text{C}_{22}\text{H}_{22}\text{O}_7$, m. p. 169—170°, and converted by *N*- NaOH into apocropodophyllin acid, $\text{C}_{22}\text{H}_{24}\text{O}_8$, m. p. 160—165° (decomp.). (I) and (II) are considered to be structural isomerides. Oxidation of (IV) with KMnO_4 gives a small amount of an acid, $\text{C}_{21}\text{H}_{18}\text{O}_9$, m. p. 213—214° (*Me* ester, m. p. 126—127°), whilst (II) is reduced by HI (*d* 1.7) in AcOH to podophyllomeronic acid, $\text{C}_{13}\text{H}_{10}\text{O}_4$, m. p. 236—237° (*Me* ester, m. p. 121—123°; *Ac* derivative, m. p. 103—104°; dinitro-derivative, darkens at 250° and decomp. slowly without melting).

H. BURTON.

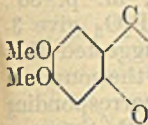
Chemistry of polyene pigments. Condensation product of benzylideneacetone. I. J. POSTOVSKI and B. P. LUGOVKIN (J. Gen. Chem. Russ., 1930, 1, 1006—1011).—Benzylideneacetone treated with KOH in EtOH gives an orange-red substance, $\text{C}_{30}\text{H}_{26}\text{O}$ (I), m. p. 247—250°, which is approx. dimeric in C_6H_6 solution. (I) gives characteristic colour reactions, forms a brownish-black bromide, and is readily oxidised in the air, giving a yellow compound, $\text{C}_{28}\text{H}_{24}\text{O}_5$, which gradually loses 2O in the dark (more rapidly on heating) but later tends to absorb it again.

G. A. R. KON.

Conjugated double linkings. XXIII. Dihydro-compound of the isomeric bixins and the electronic configuration of polyenes. R. KUHN and A. WINTERSTEIN (Ber., 1932, 65, [B], 646—651).—The isomerisation of bixin to β -bixin and of methylbixin to β -methylbixin differs from that of β -carotene to isocarotene in that it can be effected with minute amounts of I. Since dihydrobixin is obtained from bixin and β -bixin and dihydromethylbixin from methylbixin and β -methylbixin, the *cis-trans*-isomerism of the bixins is established. It is very probable that addition of the H atoms occurs at the ends of the system of conjugated double linkings as in the case of the amalgam reduction of $\omega\omega'$ -diphenylpolyenes. The views on electronic configuration of Radulescu (A., 1931, 1351) and of Wittig and Wiemer (*ibid.*, 92) are criticised; there appears no immediate reason to abandon the classical conception of double linkings

when assigning structural formulæ to the natural polyene dyes. H. WREN.

Toxicarol. III. Relation between toxicarol and the rotenone group of fish poisons. E. P. CLARK (J. Amer. Chem. Soc., 1932, 54, 1600—1602; cf. A., 1931, 1065).—Oxidation of dehydrotoxicarol (I) with KMnO_4 in COMe_2 gives rissic and 2-hydroxy-4:5-dimethoxybenzoic acids, the former being obtained in small and variable quantities. (I) boiled gently with EtOH-KOH affords an acid apparently analogous to deguelic and derric acids, oxidised by alkaline KMnO_4 to derric acid. Toxicarol contains the annexed grouping, as do rotenone, deguelin, and tephrosin.



C. J. WEST (b).

Carotene. IV. Hydrogenation of carotenes from different sources, of dihydrocarotene, and of lycopene. J. H. C. SMITH (J. Biol. Chem., 1932, 96, 35—51; cf. A., 1931, 491).—The substances were hydrogenated in a micro-apparatus with PtO freshly reduced to Pt as catalyst and with $\text{Bu}_2\text{O}+\text{AcOH}$, cyclohexane and AcOH, and *p*-menthane as solvents. Carotenes from various sources all absorb approx. 20H per mol. of pigment. Caroteneloses only one double linking on reduction by Al-Hg. Lycopene absorbs 26H per mol. (cf. A., 1928, 1016).

F. O. HOWITT.

Vegetable, fish, and insect poisons. III. Rotenone, the physiologically active constituent of *Derris elliptica*: constitution of rotenone. III. A. BUTENANDT and W. MCCARTNEY (Annalen, 1932, 494, 17—41; cf. A., 1930, 478).—Rotenone is assigned a structure [identical with that suggested by La Forge and Haller (this vol., 401)] which explains all its reactions. Formulæ are also assigned to the numerous degradation products prepared by Butenandt, Kariyone, Takei, and Haller and La Forge.

Derrisic acid is oxidised by H_2O_2 in dil. KOH at 60—100° to derric acid, m. p. 165° (Me_2 , m. p. 66°, and Et_2 , m. p. 62°, esters). Rissic acid, m. p. 257° (Me_2 ester, m. p. 84°), distils unchanged at 265—270°/0.4 mm.; when heated at atm. pressure and then distilled, decarboxyrissic acid, m. p. 115° (Me ester, m. p. 45°), is obtained. Oximation of dihydro-rotenone in alkaline solution (cf. *loc. cit.*) gives the isooxime, m. p. 201°. Rotenonone is converted by boiling 20% MeOH-KOH into rotenononic acid and 10—15% of derritol. Netoric acid, obtained by oxidation of rotenol with H_2O_2 in 5% EtOH-KOH at 100° (bath) (cf. La Forge and Smith, A., 1931, 227), exists in two interconvertible modifications, m. p. 87° and 131°. Rotenone is oxidised by dil. HNO_3 to an unidentified acid, $\text{C}_8\text{H}_3\text{O}_8\text{N}_3$ (?), m. p. 212—213°.

H. BURTON.

Isoprene and caoutchouc. XXXVI. Constitution of caoutchouc. H. STAUDINGER (Angew. Chem., 1932, 45, 276—280, 292—295).—The isoprene residues in caoutchouc (I) are in long chains. The primary colloid particles, which exist in a dil. solution, are identical with mols. Homopolar mol. colloids, such as (I), are differentiated from heteropolar, micellar colloids, such as soap. Work on the mol. wt. of (I) is reviewed.

E. S. HEDGES.

Physico-chemical properties of terpin hydrate. N. SCHOORL (Natuurwetensch. Tijds., 1932, 14, 35—40).—The behaviour of terpin hydrate on dehydration and rehydration confirms the view that the compound is a true monohydrate. The dissociation pressure at 15° is about 0.6 mm. Dehydration is complete but slow at 70—80°. Terpin (m. p. 105°) and its hydrate form at 95° a eutectic containing 10% of the hydrate; no second hydrate appears to exist. The phase diagram of the system terpin hydrate- H_2O indicates an upper crit. solution temp. of 158°, and a lower of 59°, the composition in both cases being 45—50% terpin hydrate. The m. p. of terpin hydrate falls on addition of H_2O to 114° (20% H_2O), when the system becomes heterogeneous; homogeneity is reattained at 84% H_2O . H. F. GILLBE.

Δ^1 -Dehydroisopulegol from citral. O. ZEITSCHTEL and H. SCHMIDT (J. pr. Chem., 1932, [ii], 133, 370—373).— Δ^1 -Dehydroisopulegol (Δ^1 -4-isopropylidenemethylcyclohexen-3-ol) (I) [modified prep. (25—30% yield) from citral], b. p. 218—219° (acetate, b. p. 234—235°), has the physical consts. recorded (A., 1899, i, 768) but an odour of isopulegol. The presence of two ethylenic linkings is proved by titration with Br. The dihydrochloride, an oil, with 2% aq. KOH gives an oil and a few crystals. (I) loses H_2O when heated with acids or, better, a trace of I, to yield *p*-cymene. (I) with CrO_3 in COMe_2 gives much hydrocarbon and a little ketone, an oil (semicarbazone, m. p. 193°; oxime), and when reduced (Ni) affords a mixture of menthols, b. p. 214—215°, containing neomenthol and giving isomenthone on oxidation. Attempts at partial reduction of (I) failed. R. S. CAHN.

Disubstituted derivatives of eucalyptol. A. SOLDI (Gazzetta, 1932, 62, 221—227).— α -Bromoketocineole with $\text{NH}_2\text{OH.HCl}$ gives an oxime, $\text{C}_{10}\text{H}_{16}\text{O}_2\text{NBr}$, m. p. 165°, which on further treatment with NH_2OH in presence of anhyd. NaOAc gives the hydroxylamine-oxime, $\text{C}_{12}\text{H}_{21}\text{O}_5\text{N}_2$, m. p. 83°, and with gaseous NH_3 in anhyd. Et_2O the amino-oxime [monohydrate, m. p. 226°; chloroplatinate, m. p. 252° (decomp.); hydrochloride dihydrate] of ketocineole and a substance m. p. 232°, and with piperidine gives the oxime, m. p. 173°, of α -piperodinoketocineole.

E. E. J. MARLER.

New solid *dl*-fenchyl alcohol from American pine oil. O. ZEITSCHTEL and K. TODENHÖFER (J. pr. Chem., 1932, [ii], 133, 374—376).—The alcohols from American pine oil yield a mixture of borates; a portion of this, m. p. 119—122°, is stable to aq. NaOH but with hot KOH-EtOH gives a new *dl*-fenchyl alcohol (I), b. p. 201.4°/770 mm., m. p. 38—39°, $[\alpha]_D$ -0.20° (acetate, m. p. -0.5°, b. p. 79°/5 mm., $[\alpha]_D$ -0.7°; formate, m. p. 21°, b. p. 207—208°, $[\alpha]_D$ -0.11°; phenylurethane, m. p. 104°), which with Beckmann's mixture affords *dl*-fenchone, $[\alpha]_D$ +2.25°. The optically active constituent could not be removed. (I) is thus an isomeride (H, OH) of the known *dl*-fenchyl alcohol. 1-Fenchyl formate has m. p. -13°, b. p. 77°/6 mm., $[\alpha]_D$ -76°. R. S. CAHN.

Orientation in the furan nucleus. 2-Methyl-3-furoic acid. H. GILMAN, R. R. BURTNER, and E. W. SMITH (Rec. trav. chim., 1932, 51, 407—410).—Et 5-nitro-2-methyl-3-furoate [from Et 2-methyl-3-

furoate (modified prep.)] is hydrolysed by 33% H_2SO_4 or, better, 20% HCl to 5-nitro-2-methyl-3-furoic acid (I), m. p. 154—154.5°, also obtained from 2-methyl-3-furoic acid by fuming HNO_3 in Ac_2O at -10° . (I) with quinoline and a little Cu-bronze at 200—205° affords 5-nitro-2-methylfuran (thereby proving the position of the NO_2 -group) and with Br gives 5-bromo-2-methyl-3-furoic acid, m. p. 118°. R. S. CAHN.

β -Substituted furans. H. GILMAN, R. R. BURTONER, and G. F. WRIGHT (J. Amer. Chem. Soc., 1932, 56, 1696).—Furan-3-carboxylic acid is obtainable by pyrolysis of furan-2:4-dicarboxylic acid. 3-Iodo-2:5-dimethylfuran readily forms a Grignard reagent. C. J. WEST (b).

Introduction of furylalkyl groups by means of sulphonic esters. H. GILMAN and R. E. BROWN (Iowa State Coll. J. Sci., 1931, 6, 11—15).—Toluene-*p*-sulphonyl chloride with tetrahydrofurfuryl alcohol afforded the toluene-*p*-sulphonate, from which volatile impurities were removed at 145—150°/11 mm. The ester reacted with $CH_2Ph-MgCl$ to give tetrahydrofurfurylphenylmethane. Tetrahydrofurfuryl chloride, bromide, and iodide were prepared.

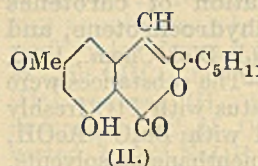
CHEMICAL ABSTRACTS.

Isomerism of tetrahydropyrones. R. CORNUBERT and P. ROBINET (Compt. rend., 1932, 194, 1081—1083).—The pyrone-like compound (I), m. p. 175°, of 2:6-dimethylcyclohexanone (A., 1928, 416) is converted by dil. HCl at 125—140° into $PhCHO$, the tetrahydropyrone (II), m. p. 206° (*loc. cit.*, m. p. 197—198°), and the original ketone, which with $PhCHO$ and HCl at -15° gives only the tetrahydropyrones, m. p. 175° and m. p. 216° (III) (*loc. cit.*). Similar hydrolysis of (II) occurs only partly and with difficulty, giving a ketone from which a small quantity of (II) can be regenerated. Hydrolysis of (III) gives $PhCHO$ and the ketone, the quantity available being too small for further investigation. The isomerism of these derivatives is discussed and, in this connexion, it is found that condensation of acetonedicarboxylic acid with $PhCHO$ in the presence of HCl affords 2:6-diphenyltetrahydropyrone, m. p. 131°, and a geometrical isomeride, m. p. 76°, with the same chemical properties. J. W. BAKER.

Hydroxy-carbonyl compounds. VI. Application of the Simonis reaction to *p*-cresol. A. ROBERTSON and W. F. SANDROCK (J.C.S., 1932, 1180—1184).—Condensation of *p*-cresol and Et acetoacetate in the Simonis reaction gives 4:6-dimethylcoumarin, m. p. 152° (lit. 148°), which is converted by $NaOH$ and subsequent methylation into 2-methoxy- β :5-dimethylcinnamic acid, m. p. 120°, oxidised to 2-methoxy-5-methylacetophenone (semicarbazone, m. p. 201—202°). *p*-Cresol and Et α -ethylacetoacetate with 84% H_2SO_4 afford 4:6-dimethyl-3-ethylcoumarin, m. p. 106°, converted into 2-methoxy- β :5-dimethyl- α -ethylcinnamic acid, m. p. 113°, but with P_2O_5 , mainly 2:6-dimethyl-3-ethyl-1:4-benzopyrone, b. p. 140—158°/6 mm., is obtained, which with piperonal and $NaOEt$ yields 2-(3':4'-methylenedioxy)styryl-6-methyl-3-ethyl-1:4-benzopyrone, m. p. 154°, also obtained from the product of ring closure of 2-hydroxy-5-methyl-*n*-butyphenone with $NaOAc$ and Ac_2O . 4-Phenyl-6-methyl-

coumarin, m. p. 131°, is prepared from *p*-cresol, Et benzoylacetate, and H_2SO_4 , but $NaOAc$ and Ac_2O give with 2-hydroxy-5-methylbenzophenone the acetate, m. p. 65°, of the ketone. 6-Methylflavone and its 3-*Bz* derivative, m. p. 184°, result from vigorous benzoylation of 2-hydroxy-5-methylacetophenone, and also in small amount from *p*-cresol, Et benzoylacetate, and P_2O_5 together with a compound, m. p. 86°. *p*-Cresol, Et α -chloroacetoacetate, and P_2O_5 give 3-chloro-4:6-dimethylcoumarin. It is suggested that the only trustworthy method of detecting the coumarin structure is by conversion into the corresponding 1-*O*-methylcinnamic acid. F. R. SHAW.

Lichen substances. XIII. Olivetoric acid. II. Y. ASAHINA and J. ASANO (Ber., 1932, 65, [B], 584—586; cf. this vol., 521).—Short treatment of olivetoric acid with diazomethane in Et_2O affords the Me ester of the Me_2 ether (I), m. p. 132°, hydrolysed by 95% HCO_2H to olivetonide Me ether (II), m. p. 57°, obtained also from olivetonide and diazomethane. Treatment of (I) with $KOH-EtOH$ affords olivetonide Me ether and Me olivetolcarboxylate



o-Me ether, (corresponding acid, m. p. 105°). The constitution of olivetoric acid (*loc. cit.*) is thus confirmed. H. WREN.

Hydroxychrysin (5:7:8-trihydroxyflavone, norwogonin). M. NIENENSTEIN (Acta Phytochim., 1932, 6, 173—175).—5:7:8-Trihydroxyflavone, m. p. 227—228° (this vol., 64), is probably a hydrate of the anhyd. form, m. p. 305° (A., 1912, i, 292), and is identical with hydroxychrysin. R. S. CAHN.

5:7:8-Trihydroxyflavone. S. HATTORI (Acta Phytochim., 1932, 6, 177—178).—A reply to Nierenstein (cf. preceding abstract). 5:7:8-Trihydroxyflavone (synthetic or from wogonin), recryst. from $AcOH$ and a few drops of H_2O , contains $1H_2O$ (lost above 100° in vac.), but the hydrated and anhyd. forms melt at 227—228°. It is not identical with hydroxychrysin. R. S. CAHN.

Spectrography of flavones. V. Relations between absorption of light and hydroxyl substituents among flavone derivatives. S. HATTORI (Acta Phytochim., 1932, 6, 131—154; cf. this vol., 64).—The absorption spectra, partly new, of many hydroxyflavones are described. It is possible by their means to determine the positions of OH groups in the flavone series. The auxochromic effect of OH groups is not affected by methylation or glucoside formation, but is destroyed by acylation. Resacetophenone Me_2 ether, Me *o*-methoxybenzoate, and Na at 120—125° give 2:4:2'-trimethoxybenzoylacetophenone, m. p. 96—97°, whence by HI first 7:2'-dimethoxy-, m. p. 176—177°, and then 7:2'-dihydroxy-flavone, m. p. above 300°, were obtained. Resacetophenone Me ether and *m*-methoxybenzaldehyde in hot $KOH-EtOH$ give 2-hydroxy-4:3'-dimethoxychalcone (I), m. p. 93° after sintering at 91° (lit. 80—81°), and 7:3'-dimethoxyflavanone (II),

m. p. 104° [also obtained from (I) and 5% H₂SO₄ in hot EtOH]; (II) with PCl₅ in hot C₆H₆ affords 7:3'-*dimethoxyflavone*, m. p. 153°, which with HI gives 7:3'-*dihydroxyflavone*, m. p. 276—277°. Me gallate Me₃ ether, *o*-methoxyacetophenone, and Na at 130—135° give 2:3':4':5'-*tetramethoxybenzoylacetophenone*, m. p. 105—107°, which with HI yields 3':4':5'-*trihydroxyflavone*, m. p. above 280° (Me₃ ether, m. p. 174—175°; Ac₃ derivative, m. p. 195—196°). β-Resorcyaldehyde Me₂ ether and *o*-hydroxyacetophenone in hot NaOH-EtOH give 2-hydroxy-2':4'-*dimethoxychalkone*, m. p. 107°, which with aq. NaOH forms 2':4'-*dimethoxyflavanone*, m. p. 131—132°, whence 2':4'-*dimethoxy*-, m. p. +1.5H₂O 135°, anhyd. 221°, and 2':4'-*dihydroxyflavone*, m. p. 268—270°, were obtained. 2:4:5-*Trimethoxyacetophenone* (prepared by a Friedel-Crafts reaction), m. p. 102°, with BzOEt and Na at 120—125° yields 2:4:5-*trimethoxybenzoylacetophenone*, m. p. 104—105°, which with HI gives 6:7-dimethoxy-, m. p. 189°, and 6:7-dihydroxyflavone, m. p. 252° after sintering (anhyd. or +H₂O) [not 135° (+H₂O) (lit.)].

R. S. CAHN.

Synthetical experiments in the chromone group. VII. Synthesis of 7:8:4'-*trihydroxy*-, 7:8:3':4'-*tetrahydroxy*-, and 7:8:3':4':5'-, 5:7:3':4':5'-, and 3:7:3':4':5'-*pentahydroxyflavones*. I. C. BADHWAR, K. S. KANG, and K. VENKATARAMAN (J.C.S., 1932, 1107—1112).—2'-*Acetoxy-4:3':4'-trimethoxychalkone dibromide*, m. p. 133°, and KOH give 7:8:4'-*trimethoxy*-, m. p. 189—190°, demethylated to *trihydroxyflavone*, m. p. 299—300° (decomp.) (Ac₃ derivative, m. p. 183°). 2'-*Acetoxy-3:4:3':4'-tetramethoxychalkone dibromide*, m. p. 118°, 7:8:3':4'-*tetramethoxy*-, m. p. 198—199°, and *tetrahydroxyflavone* (I), m. p. 309—310° (decomp.) (Ac₄ derivative, m. p. 218°), are similarly prepared. Et vertrate, gallacetophenone Me₃ ether, and Na yield 2:3:4:3':4':5'-*pentamethoxy-ω-benzoylacetophenone*, m. p. 105°, which gives (I) on treatment with HI. 2:3:4:3':4':5'-*Hexamethoxy-ω-benzoylacetophenone*, m. p. 125°, and 7:8:3':4':5'-*pentahydroxyflavone*, m. p. above 345° (Ac₅ derivative, m. p. 263°), are similarly prepared. Trimethylgallic anhydride and K trimethylgallate with *ω*-methoxyresacetophenone and phloracetophenone give, respectively, 7-hydroxy-3:3':4':5'-*tetramethoxy*-, m. p. 246° (Ac derivative, m. p. 146°), demethylated to 3:7:3':4':5'-*pentahydroxy*-, m. p. 310—312° (decomp.) (Ac₅ derivative, m. p. 175—176°), and 5:7-dihydroxy-3':4':5':5'-*trimethoxy*-, m. p. 264—265°, demethylated to 5:7:3':4':5'-*pentahydroxyflavone*, decomp. about 310°. The colour reactions of the above flavones are described.

F. R. SHAW.

Constitution of dye of toad-flax petals (*Linaria vulgaris*). L. SCHMID and W. RUMPEL (Monatsh., 1932, 60, 8—25).—The hydrocarbon previously isolated from the degradation products of the aglucone (A., 1931, 738) is found to have been present in the original dye, and is hentriacontane, m. p. 67—69°. Alkaline degradation of the hydrocarbon-free aglucone gives anisic acid and unidentified phenolic substances. Demethylation (2Me) with HI gives scutellareine. Acetylation gives the Ac₂

derivative of 6:4'-dimethylscutellareine (cf. A., 1930, 1295); this Me ether, m. p. 218°, and the aglucone, m. p. 201°, are dimorphic, the latter being formed by hydrolysis of the Ac₂ derivative or by prolonged heating of the former at its m. p., and being converted into the former by crystallisation from EtOH. The original glucoside is unaffected by diazomethane. It is accompanied in the petals by mannitol.

H. A. PIGGOTT.

A rearrangement in the flavone series. F. WESSELY and F. KALLAB (Monatsh., 1932, 60, 26—31).—Interaction of 1:2:3:5-C₆H₂(OMe)₄, AlCl₃, and AcCl gives 2-hydroxy-3:4:6-trimethoxyacetophenone and a dihydroxydimethoxyacetophenone, m. p. 160—162° (cf. A., 1911, i, 211); the former on condensation with Na or K anisate and anisic anhydride gives the expected 5:7:8:4'-*tetramethoxyflavone*, m. p. 206—207°, identical with the product of methylation of 7-hydroxy-5:8:4'-*trimethoxyflavone* (cf. A., 1930, 1295). This on demethylation gives scutellareine and not 5:7:8:4'-*tetrahydroxyflavone* as stated by Hattori (this vol., 64). Condensation of 2:4-dihydroxy-3:6-dimethoxyacetophenone with Na anisate and anisic anhydride gives 5:7-dihydroxy-6:4'-*dimethoxyflavone*, dimorphic, m. p. 218° (from EtOH), 206° (fused or sublimed) (cf. A., 1930, 1295).

H. A. PIGGOTT.

Dye of yellow dahlias. L. SCHMID and A. SEEBALD (Monatsh., 1932, 60, 32—49).—The yellow dye, C₁₅H₁₀O₅, decomp. 324° (darkens >315°; sublimes >165°/vac.), is extracted from the petals with EtOH, separated from apigenin by extraction with Et₂O, and, after treatment with solvents, purified by sublimation. It is not a glucoside, is free from OMe groups, and gives negative results on distillation with Zn dust. Ac₂O at its b. p. gives a substance, m. p. 178°, and in presence of NaOAc a substance, decomp. 345—350°; both are produced in small yields and fail to regenerate the original dye on hydrolysis. A Me₂ ether (I), m. p. 175.5°, is formed with Me₂SO₄ and alkali, but the dye has three OH groups (Zerevitinov). Fusion of the dye with NaOH at 220° in H₂ gives *p*-hydroxybenzoic acid and unidentified phenols (in poor yield); it is therefore most probably a flavone derivative. (I) with 20% KOH in EtOH at 100° gives anisic acid and unidentified phenols.

H. A. PIGGOTT.

Thioxanthhydrol: action of acids. C. FINZI (Gazzetta, 1932, 62, 211—218).—Gaseous HCl converts thioxanthhydrol (I) in dry Et₂O into the red thioxanthonium chloride (J.C.S., 1911, 99, 158), which with NH₃ in dry Et₂O gives *dithioxanthenylamine*, m. p. 168°, but the main product is a mixture of thioxanthone and thioxanthene. The same mixture is obtained by the action on (I) of AcOH, dil. HCl, or heat. Conc. H₂SO₄ gives only thioxanthone.

E. E. J. MARLER.

Action of Grignard reagents on pyrrolones. General synthesis of 1:2:5-trisubstituted pyrrolones. R. LUKEŠ (Coll. Czech. Chem. Comm., 1932, 4, 181—192).—The action of the Grignard reagent on pyrrolones gives the trisubstituted pyrroles with some *γ*-diketones and pyrrolines as by-products. MgMeBr and 1:5-dimethylpyrrol-2-one, subsequently treated with NH₂Me, afford 1:2:5-trimethylpyrrole,

and similarly 1-methyl-5-ethylpyrrol-2-one (I) gives 1:2-dimethyl-5-ethylpyrrole, b. p. 186—187°/761 mm., but with MgEtBr yields 1-methyl-2:5-diethylpyrrole, b. p. 89.0—89.2°/13 mm., 1-methyl-2:5:5-triethyl- Δ^2 -pyrroline, b. p. 116°/10 mm., and dipropionylethane. (I) and $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ afford dibenzyl and an inseparable mixture of diketone and pyrrole, converted by NH_2Me into 5-benzyl-1-methyl-2-ethylpyrrole, b. p. 162°/10 mm., obtained also mixed with diketone by the action of MgEtBr on 5-benzyl-1-methylpyrrol-2-one (II). MgMeBr and (II) form 5-benzyl-1:2-dimethylpyrrole, m. p. 50—51°, and 1:2:2-trimethyl-5-benzyl- Δ^2 -pyrroline (isolated as the perchlorate, m. p. 188°). (II) and $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ yield 2:5-dibenzyl-1-methylpyrrole, m. p. 92—93°, and no diketone.

F. R. SHAW.

Basis for the physiological activity of -onium compounds. X. Heterocyclic -onium compounds. R. R. RENSHAW and E. W. SHAND (J. Amer. Chem. Soc., 1932, 54, 1474—1476).—Methyl- β -phenoxyethylpiperidinium bromide, m. p. 112—113° (all m. p. are corr.), and iodide, m. p. 121.2°; methyl- β -phenoxyethylpyrrolidinium iodide, m. p. 86.5—87.5°; methyl-, m. p. 119—121°, and ethyl-, m. p. 97—99°, - β -phenoxyethylpyrrolinium iodides are prepared from the requisite *N*- β -phenoxyethyl-base and alkyl iodide. β -Phenoxyethylpyridinium and 3-hydroxy- β -phenoxyethylpyridinium bromides, m. p. 80—83° and 126—127°, respectively, and 2- and 3-acetamidopyridine methiodides, m. p. 177° and 220—221°, respectively, are also prepared. These compounds have no pronounced effect on the autonomic nervous system.

C. J. WEST (b).

Cationoid reactivity of aromatic compounds. I. W. BRADLEY and R. ROBINSON (J.C.S., 1932, 1254—1263).—The action of $\text{C}_5\text{H}_{11}\text{N}$, and NaNH_2 gives (a) with PhNO_2 , *p*-nitrophenylpiperidine, m. p. 103—103.5°; (b) with 1-nitronaphthalene, 1-nitro-4-piperidinonaphthalene, m. p. 73.5—74° [reduced to 1-amino-, m. p. 78—79° (*Bz* derivative, m. p. 213—214°)], and a piperidino- α - β -dinaphthazine, m. p. 257—258°; (c) with *p*-nitrotoluene, 4:4'-dinitrodibenzyl; (d) with 8-nitroquinoline, diluted with C_6H_6 , 8-nitroquinolylpiperidine (possibly 4 or 7), m. p. 131.5—132.5°; (e) with 5-chloro-8-nitroquinoline, 8-nitro-5-piperidinoquinoline, m. p. 105.5—106.5°; (f) with 2-chloro-8-nitroquinoline, 8-nitro-2-piperidinoquinoline, m. p. 87°; and (g) with benzanthrone, piperidinobenzanthrone, m. p. 176.5—178°. With liquid NH_3 and NaNH_2 , PhNO_2 forms a base, $\text{C}_{12}\text{H}_8\text{ON}_2$, m. p. 215° (decomp.), and a phenolic base, m. p. 230—231°. General cationoid reactions are discussed.

F. R. SHAW.

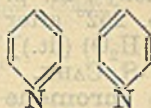
Mercuric iodide compound of pyridine. II. V. V. ZAPOLSKI (U.S.S.R. State Inst. Tobacco Inv. Bull., 1931, No. 81, 113—117; cf. A., 1930, 1594).—The following compounds are described: $2\text{C}_5\text{H}_5\text{N}\cdot\text{HgI}_2$, m. p. 103°, and $\text{C}_5\text{H}_5\text{N}\cdot\text{HgI}_2$, m. p. 87°. Unstable products containing higher proportions of HgI_2 and apparently consisting of mixtures of $\text{C}_5\text{H}_5\text{N}\cdot 2\text{HgI}_2$ and $\text{C}_5\text{H}_5\text{N}\cdot 3\text{HgI}_2$ were also obtained. At room temp., the compounds containing HI (*loc. cit.*) lose all their HI and part of their $\text{C}_5\text{H}_5\text{N}$ when treated with alkali, giving $\text{C}_5\text{H}_5\text{N}\cdot\text{HgI}_2$. The latter has the

normal mol. wt. in freezing C_6H_6 but $2\text{C}_5\text{H}_5\text{N}\cdot\text{HgI}_2$ dissociates. T. H. POPE.

Behaviour of the pyridine group on electrochemical oxidation. II. Picoline. M. YOKOYAMA (Bull. Chem. Soc. Japan, 1932, 7, 69—72).—The oxidation of α -picoline, dissolved in dil. H_2SO_4 , at a Pb—PbO₂ anode gave rise to picolinic acid, together with smaller quantities of HCO_2H , AcOH , NH_3 , HNO_3 , picolylalkine, CO, and CO_2 . Using a Pt anode, the same products were obtained in much smaller yields. Picolinic acid under the former conditions gave CO, CO_2 , HCO_2H , NH_3 , CH_2O , NH_2Me , NHMe_2 , and NMe_3 . D. R. DUNCAN.

New type of isomerism in the pyridine series. I. A. KIRPAL and W. BÖHM (Ber., 1932, 65, [B], 680—682).—Oxidation of 2- and 4-aminopyridine with 30% H_2O_2 and fuming H_2SO_4 affords 2- and 4-nitropyridine, m. p. 50°. Oxidation of 2-aminopyridine with KOCi yields 2:2'-azopyridine, m. p. 87°, in addition to the known isomeride, m. p. 81°, which differ in appearance, m. p., solubility, and lower crit. solution temp., but show identical absorption spectra. The isomerism is accounted for in accordance with (I). Reduction of 2-nitropyridine with Na_3AsO_3 and NaOH gives exclusively the compound m. p. 87°. H. WREN.

[Halogeno-derivatives of] pyridine[carboxylic acids]. M. DOHRN and P. DIEDRICH (Annalen, 1932, 494, 284—302).—3:5-Di-iodochelidamic acid (I) [chloride, m. p. 149°; *Me*, m. p. 173°, *Et* (II), m. p. 169°, and *benzyl*, m. p. 200° (decomp.), esters] and Me_2SO_4 in aq. KOH at 35° give 3:5-di-iodo-*N*-methylchelidamic acid (III), m. p. 174° (decomp.) (*Me* ester, m. p. 194—195°), whilst the *Ag* salt of (II) and *MeI* in xylene afford the *Et* ester, m. p. 100—101°, of 3:5-di-iodo-*O*-methylchelidamic (3:5-di-iodo-4-methoxy-pyridine-2:6-dicarboxylic) acid, decomp. 176°. 3:5-Di-iodo-4-ethoxy-, m. p. 174° (decomp.) (*Me* ester, m. p. 131°), -propoxy-, m. p. 156° (decomp.) (*Me* ester, m. p. 89°), -butoxy-, m. p. 145° (decomp.) (*Me* ester, m. p. 82°), and -benzyloxy-, m. p. 167° (decomp.) (*Me* ester, m. p. 120°), -pyridine-2:6-dicarboxylic acids are prepared similarly. (III) heated at 170° gives 3:5-di-iodo-*N*-methyl-4-pyridone, m. p. 214—215°, also prepared from 3:5-di-iodo-4-pyridone (IV), m. p. 321° (decomp.), and Me_2SO_4 in aq. KOH ; (IV) is obtained from 4-pyridone and ICl in dil. HCl and by hydrolysis of its *N*-Ac derivative, m. p. 245° (decomp.) [(from (I) and boiling Ac_2O]. (I) and (IV) with ClSO_3H give the corresponding *N*-sulpho-derivatives, m. p. 210° (decomp.) and 183° (decomp.), respectively, hydrolysed by H_2O to H_2SO_4 and (I) and (IV). 3:5-Di-iodo-4-pyridone-*N*-acetic acid, m. p. 240° (decomp.), is prepared from (IV) and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$. 4-Pyridone-2-carboxylic acid (V) and I in aq. KOH give the 3:5- I_2 -derivative, decomp. 250° [*N*-*Me*, m. p. 159° (decomp.), and *N*- $\text{CH}_2\cdot\text{CO}_2\text{H}$, m. p. 223° (decomp.), derivatives]; 2-pyridone-6-carboxylic acid similarly affords the 3:5- I_2 -derivative, decomp. 272° [*N*-*Me* derivative, m. p. 194° (decomp.)], also formed by iodination of 2-pyridone-5:6-dicarboxylic acid. 3:5-Dichloro-, m. p. above 300° (*N*-*Me* derivative, m. p. 166°), and 3:5-dibromo-, m. p. above 300°



(I)

[*N-Me* derivative, m. p. 170° (decomp.)], 4-pyridone-2-carboxylic acids are obtained by halogenation of (V). Et 3:5-dichlorochelidamate, m. p. 96°, and PCl₅ give the *Et* ester, m. p. 35°, of 3:4:5-trichloropyridine-2:6-dicarboxylic acid, decomp. 150°. 4-Chloro-, m. p. 232° (decomp.) (*Et* ester, m. p. 111°), and 4-bromo-, m. p. 186° (decomp.) (*Et* ester, m. p. 98—99°), 3:5-di-iodopyridine-2:6-dicarboxylic acids are prepared from (II) and PCl₅+POCl₃ and PBr₅. The *Et* ester of 3:4:5-tribromopyridine-2:6-dicarboxylic acid, m. p. 180° (decomp.), has m. p. 67°.

3:4:5-Trichloropyridine, m. p. 76—77°, from 3:5-dichloro-4-pyridone, PCl₅, and POCl₃ at 125°, with EtOH-KHS gives 3:5-dichloro-4-thiopyridine, m. p. 188°, oxidised by alkaline KMnO₄ to 3:5-dichloropyridine-4-sulphonic acid, m. p. above 300°. 4-Chloro-3:5-dibromo-, m. p. 98°, and 4-chloro-3:5-di-iodo-, m. p. 175°, -pyridines are similarly converted by way of 3:5-dibromo-, m. p. 222°, and 3:5-di-iodo-, m. p. 206° (decomp.), 4-thiopyridines into 3:5-dibromo- (VI) and 3:5-di-iodo- (VII), decomp. 308°, -pyridine-4-sulphonic acids. 3:5-Dibromo- and 3:5-di-iodo-pyridine-2-sulphonic acids, both decomp. above 300°, are prepared similarly. (VI) and aq. NH₃ (d 0.91) at 130° give 3:5-dibromo-4-aminopyridine, m. p. 169—170°; 3:5-dibromo-4-anilino-, m. p. 167°, and 4-*o*-carboxyanilino-, m. p. 252° (as *Et* ester, m. p. 105—106°), -pyridines are formed, using NH₂Ph and *o*-NH₂C₆H₄·CO₂Et, respectively. When an aq. solution of (VI) is heated, 3:5:3':5'-tetrabromo-*N*-4'-pyridyl-4-pyridone, m. p. above 300°, and SO₂ are formed. 3:5:3':5'-Tetraiodo-*N*-4'-pyridyl-4-pyridone, decomp. above 300°, is obtained similarly from (VII).

H. BURTON.

Action of phosphorus pentachloride on acetanilide. O. G. BACKBERG (J.C.S., 1932, 1138—1142).—The action of 1, 2, or 3 mols. of PCl₅ on NPhAc gives, respectively, diphenylchlorovinylacetamide and a small amount of 4-anilinoquinoline; 3-chloro-4-anilino-2-chloromethylquinoline hydrochloride, (I), m. p. 243—245° (decomp.) (lit. 222°), the free base having m. p. 135—136° (lit. about 130°); in the cold, (I) and diphenylacetamide, and on heating, *o*-dichloroacetanilide (cf. Michael, A., 1887, 481). An explanation of the reactions is given.

F. R. SHAW.

Quinoline derivatives. XXXIX. H. JOHN (J. pr. Chem., 1932, [ii], 133, 350—354; cf. this vol., 523).—By interaction with the appropriate base 4-bromo-2-phenylquinoline affords 4-ethylamino-, m. p. 82° (EtOH at 160—170°), 4-*N,N'*-dimethyl-*p*-phenylenediamino-, m. p. 177° (amyl alcohol at 100°), and 4-(4'-hydroxy-5'-carboxyanilino)-, m. p. 283° (boiling amyl alcohol), 2-phenylquinoline, and *NN'*-di-(2-phenylquinolyl-4-)ethylenediamine, m. p. above 300° (EtOH at 140—150°). Inorg. and complex salts of these bases are described.

R. S. CAHN.

Trypanocidal action of some derivatives of anil and styryl quinolines. II. C. H. BROWNING, J. B. COHEN, K. E. COOPER, and R. GULBRANSEN (Proc. Roy. Soc., 1932, B, 110, 372—377; cf. A., 1929, 1109; 1931, 763).—2-Methyl-6-acetyl-lactamidoquinoline, m. p. 141—142° (methosulphate, methochloride), from 6-amino-2-methylquinoline and acetyl-lactyl

chloride (A., 1904, i, 966) in CHCl₃, yields on deacetylation 2-methyl-6-lactamidoquinoline, m. p. 192° (methosulphate). The acetyl-lactamido-derivatives of PhCHO, m. p. 114—115°, and of 2-methylbenzthiazole, m. p. 153—155° (methosulphate), yield on appropriate condensation the 2-(*p*-aminostyryl)acetyl-lactyl and 2-(*p*-acetyl-lactamidostyryl) derivatives of aminobenzthiazole methochloride. *p*-Aminobenzaldehyde or nitrosodimethylaniline with the appropriate 2-methylquinoline at 100° in presence of piperidine yield 2-(*p*-aminostyryl)-6-acet- and -6-lact-amidoquinoline methochloride and the corresponding 2-(*p*-dimethyl-aminoanil) derivatives. Condensation of acetyl-lactamidobenzaldehyde with 6-amino-2-methylquinoline methochloride results in simultaneous hydrolysis of the Ac group, giving 2-(*p*-lactamidostyryl)-6-aminoquinoline methochloride. Similarly, 6-acetamido-2-methylquinoline methiodide yields 2-(*p*-lactamidostyryl)-6-acetamidoquinoline methiodide. Glyceric acid, treated successively with AcCl and SOCl₂, gives diacetyl-glyceryl chloride, b. p. 75—85°/15 mm., which with 6-amino-2-methylquinoline and then MeI, gives 6-diacetyl-glycerylamido-2-methylquinoline methiodide, m. p. 217—219° (decomp.). Condensation of the appropriate benzaldehyde in MeOH with piperidine yields the 2-(*p*-aminostyryl) and 2-(*p*-acetamidostyryl) derivatives of 6-glycerylamidoquinoline methochloride (methiodide), the two Ac groups of the glyceryl group being hydrolysed. 6-*R*-Amino-2-methylquinoline (methiodide), where R=octoyl, nonoyl, undecoyl, and lauryl, were prepared by treating the acid chloride with 6-amino-2-methylquinoline in AcOH at 100° for 1 hr. Condensation of these products yielded the methiodides and methochlorides of the corresponding 2-(*p*-dimethylaminoanil) derivatives. None of the above anil derivatives exhibits marked trypanocidal activity; the styryl derivatives are more active. Acetylation of the NH₂ in the quinoline nucleus does not generally increase the trypanocidal potency, but occasionally tends to produce convulsive effects.

F. O. HOWITT.

Relation between constitution, colour, and reactivity of heterocyclic compounds. Derivatives of homophthalimide. A. MEYER and R. VITTENET (Ann. Chim., 1932, [x], 17, 272—411).—Indene with K₂Cr₂O₇ and hot H₂SO₄ gives a 65% yield of homophthalic acid and a little indanone. The prep. of homophthalimide (I) is modified. With the appropriate diazo-compound in aq. Na₂CO₃ at 0° 2:4-dihydroxyquinoline affords 3-benzene-, m. p. 263—264°, -*o*-chlorobenzene-, decomp. 284—285°, -*m*- and -*p*-nitrobenzene-, m. p. 295—296° (decomp.) and 332—333° (decomp.), respectively, -*o*- and -*p*-toluene-, m. p. 267—268° (decomp.) and 268—269° (decomp.), respectively, -*o*- and -*m*-nitro-*p*-toluene-, m. p. 282—284° (decomp.) and 312—314° (decomp.), respectively, -*m*-xylene-, m. p. 264—265°, -1- and -2-naphthalene-, m. p. 267—268° and 264°, respectively, -*m*-carboxybenzene-, m. p. 308—310° (decomp.), -*azo*-2:4-dihydroxyquinoline, *di*-(2:4-dihydroxyquinoline-3-*azo*)-*pp'*-diphenyl, decomp. above 320°, -*di*-*o*-tolyl, m. p. above 320° (decomp.), and -*di*-*o*-anisyl, decomp. above 320°. (I) yields similarly 4-benzene-, -*o*-chlorobenzene-, m. p. 281—283°, -*o*- and -*p*-nitrobenzene-, m. p. 276—277° and 290—291°, respectively, -*o*-

-m-, and -p-toluene-, m. p. 266—267°, 228—230°, and 240—242°, respectively, -o- and -m-nitro-p-toluene-, m. p. 270—272° and 305—307°, respectively, -m-xylene-, m. p. 260—261°, -1- and -2-naphthalene-, m. p. 283—285° (decomp.) and 262—264°, respectively, -o- and -m-carboxybenzene-, decomp. about 315° and m. p. 305—307° (decomp.), respectively, antipyrine-, m. p. 252—254° (decomp.), -homophthalimide, dihomophthalimide-4-azo-pp'-diphenyl-, ditolyl-, and -dianisyl-, decomp. above 320°, and the Na salts of the following acids: homophthalimide-4-azo-benzene-p-sulphonic, -m-xylene-o-sulphonic, -β-naphthol-6 : 8-disulphonic, -naphthionic, -naphthol-2 : 4-disulphonic acid, and -primuline. Substantive dyes are produced by addition of (I) to an alkaline solution of tetrazotised benzidine, tolidine, and dianisidine, already coupled once (in both acid and alkaline solution, when different products result) with H, G, J, naphthionic, and Neville and Winther's acid, and with benzidine already coupled once with salicylic and Schaeffer's acid and 2-p-nitrobenzeneazo-H acid. (I), when heated with the appropriate primary amine, gives at least 75% yields of N-phenyl-, m. p. 191° (lit. 188°) [oximino-derivative, m. p. 234—236° (decomp.)], -p-tolyl-, m. p. 173° (oximino-derivative, decomp. 241—243°), -α- and -β-naphthyl-, m. p. 212° and 220°, respectively, -homophthalimide; these substances are fairly readily hydrolysed; the oximino-derivatives are very stable. Oximinohomophthalimide decomposes at 242—243°. By means of MeI or EtI and hot KOH-EtOH were prepared N-phenyl-4 : 4-dimethylhomophthalimide, m. p. 149—150°, N-phenyl-, m. p. 146°, N-p-tolyl-, m. p. 177—178°, and N-α-naphthyl-, m. p. 224°, -4 : 4-diethylhomophthalimide; these substances have no physiological action. Coupling at 0° with diazotised NH₂Ph gives 4-benzeneazo-N-phenyl-, -p-tolyl- (m. p. 258—259°), -α- and -β-naphthyl- [m. p. 283—284° (decomp.) and 262—263°, respectively] -homophthalimide. By treatment with the appropriate NO-compound in warm EtOH were prepared p-dimethylaminophenyl-, m. p. 243°, p-diethylaminophenyl-, m. p. 196—197°, antipyrinyl-, m. p. 224—225°, p-tolylantipyrinyl-, m. p. 227—228° (decomp.), -iminophthalonimide, C₆H₄ $\left\langle \begin{array}{c} \text{C(NR)} \\ \text{CO-NH} \end{array} \right\rangle \text{CO}$, antipyrinylphthalon-N-phenyl-, m. p. 210°, -p-tolyl-, m. p. 223—224°, -α- and -β-naphthyl-, m. p. 239—240° (decomp.) after sintering at 235°, and 180—181° (decomp.), respectively, -imide; these substances are red or bluish-violet, are decomposed rapidly by dil. alkali or acid or by prolonged boiling in neutral solvents, and are immediately reduced by boiling aq. Na₂S₂O₄. By means of the appropriate aldehyde and a few drops of piperidine or NH₂Et, in hot EtOH were prepared N-phenyl-, m. p. 193—194°, N-p-tolyl-, m. p. 185—186°, N-α- and -β-naphthyl-, m. p. 225° and 204°, respectively, -4-benzylidenehomophthalimide, N-phenyl-, m. p. 244—245°, N-p-tolyl-, m. p. 245—246°, N-α- and -β-naphthyl-, m. p. 141° and 159—160°, respectively, -4-p-dimethylaminobenzylidenehomophthalimide. The antipyrinyliminohomophthalimides with hot 15% HCl give 85—90% yields of phthalonimide (II), m. p. 228—229° (lit. 224°), phthalon-phenyl- (III) (m. p. 220—221°, sublimes from 215°), -p-tolyl- (IV) (m. p. 238°, sublimes from

220°), -α-naphthyl- (V) [m. p. 239—240° (decomp.) after sintering from 200°], and -β-naphthyl- (VI) [m. p. 268—269° (decomp.)] -imide; these substances dissolve in alkali giving (probably) phthalonic acid and substituted phthalonamides. The phenylhydrazones of these phthalonimides are identical with the products of coupling (I) with diazotised NH₂Ph; the following derivatives of the phthalonimides are described (II) phenylmethylhydrazone, m. p. 242.5°, and oxime, decomp. 242—244°; (III) phenylmethylhydrazone, m. p. 204°, oxime, m. p. 234—236° (decomp.), and semicarbazone, m. p. 230—231° (decomp.); (IV) phenylmethylhydrazone, m. p. 199°, oxime, decomp. 241—243°, and semicarbazone, decomp. 236—237°; (V) and (VI) phenylmethylhydrazone, m. p. 212° and 199—200°, respectively. o-Phenylenediamine in hot EtOH gives phenazine derivatives with (II) (m. p. 267°), (III) (m. p. 238—239°), and (IV) (m. p. 232—233°).

The colours of the above compounds are discussed and considered to be in accord with analogy. The azo-dyes are considered to have the azo- rather than the hydrazone structure, excepting those from (I) itself, which are considered to be thermolabile mixtures of both forms.
R. S. CAHN.

Determination of constitution of bases obtained from protein. III. C₁₀H₁₄O₂N₂. F. WREDE (Z. physiol. Chem., 1932, 206, 146—154; cf. this vol., 284).—The base C₁₀H₁₄O₂N₂ (I) (A., 1931, 245) when boiled for a short time with dil. HCl loses 1 mol. of AcOH and forms dl-3-acetamido-2-homopiperidone, $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH-NHAc}$, m. p. 163°, which on longer boiling (4 hr. with 10% HCl) gives dl-lysine and 1 mol. of AcOH. d-Lysine by Troensegaard's method, or on heating the dihydrochloride with AcOH and AcCl to 100°, yields (I), which is therefore $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-C(NHAc)-C(N)Me}$. d-Ornithine similarly gives a compound, C₉H₁₂O₂N₂ (chloroaurate, darkens at 175°, m. p. 184°), which on hydrolysis yields dl-3-acetamido-2-piperidone and finally ornithine.
J. H. BIRKINSHAW.

Derivatives of 4 : 5-diketopyrazoline. F. D. CHATTAWAY and A. ADAIR (J.C.S., 1932, 1022—1026; cf. A., 1927, 776).—2 : 5-Dichlorophenylhydrazone hydrochloride and dihydroxytartaric acid give diketosuccinic acid 2 : 5-dichlorophenylosazone (I), m. p. 195° (decomp.), converted by Ac₂O into the anhydride, m. p. 233°. Diketosuccinophenylhydrazone 2 : 5-dichlorophenylosazone, m. p. 286°, is obtained from the corresponding anhydride and NPh-NH₂. (I) or its anhydride and EtOH-HCl form Et 4 : 5-diketo-1-(2' : 5'-dichlorophenyl)pyrazoline-3-carboxylate 4-(2'' : 5''-dichlorophenylhydrazone) (II), m. p. 213° [acid, m. p. 214° (decomp.)], also obtained by the action of EtOH-HCl on Et diketosuccinate 2 : 5-dichlorophenylosazone, m. p. 207°, which may be prepared from the corresponding hydrazone, m. p. 101° (formed by the action of Et oxalacetate on diazotised 2 : 5-dichloroaniline). Diketosuccinic acid 2 : 4 : 5-trichlorophenylosazone and its anhydride, m. p. 295—300°, are similarly prepared. Diazotised trichloroaniline and Et oxalacetate afford the hydrazone,

converted into *Et diketosuccinate* 2:4:5-trichlorophenylosazone, m. p. 224°, forming with EtOH-HCl, 4:5-diketo-1-(2':4':5'-trichlorophenyl)pyrazoline-4-(2'':4'':5'':trichlorophenylhydrazone), m. p. 308—310° (decomp.), with elimination of the CO₂H group. *Carbethoxyglyoxal-2:4:5-trichlorophenylhydrazone*, m. p. 118°, prepared from diazotised trichloroaniline and Et sodioformylacetate, gives the *osazone*, m. p. 242°, which cannot be hydrolysed; the corresponding *carboxyglyoxal-2:4:5-trichlorophenylosazone*, m. p. 284°, is obtained from dibromopyruvic acid and 2:4:5-trichlorophenylhydrazine hydrochloride.

F. R. SHAW.

Fission of the glyoxaline ring in a base C₉H₁₁ON₃ prepared from protein. F. WREDE and G. FEUERRIEGEL (Z. physiol. Chem., 1932, 205, 198—200; cf. this vol., 284).—The compound, m. p. 185°, formed by the action of *m*-nitrobenzoyl chloride on the base C₉H₁₁ON₃ (A., 1931, 245) is 4-[βγ-di-(*m*-nitrobenzamido)-Δ^β-propenyl]-2:5-dimethylloxazole. BzCl similarly yields 4-[βγ-di(benzamido)-Δ^β-propenyl]-2:5-dimethylloxazole, m. p. 172° (cf. Windaus, A., 1910, i, 283). The presence of a glyoxaline ring in the base is thus confirmed.

J. H. BIRKINSHAW.

Chloroaurates of histamine and glyoxaline. F. HORN (Z. physiol. Chem., 1932, 207, 111—112).—When ordinary histamine chloroaurate, B₂HAuCl₄, is dissolved in hot H₂O and rapidly cooled, an irregular *chloroaurate*, B₂HAu₂Cl₅, sinters 165—166°, decomp. 179—182°, is formed. This seems to be a characteristic of the glyoxaline ring, since ordinary iminazole chloroaurate, B₂HAuCl₄, on similar treatment gives an irregular *chloroaurate*, B₂AuCl₃, decomp. 190°.

J. H. BIRKINSHAW.

Substituted piperazines. I. 2:5-Dimethyl- and tetramethyl-piperazines. II. Bistetramethylenepyrazine and bistetramethylenepiperazine. M. GODCHOT and M. MOUSSERON (Bull. Soc. chim., 1932, [iv], 51, 349—360, 360—372).—I. Reduction of 2:5-dimethylpyrazine by H₂ in presence of Ni at 150—155° affords the *α*- or *trans*-piperazine, m. p. 118°, and no trace of the *cis*-compound, but in presence of Pt a small amount of *cis*- is also formed, a similar result being obtained when oximinoacetone is hydrogenated with Pt as catalyst. Tetramethylpyrazine cannot be reduced in presence of Ni, but with Pt two tetramethylpiperazines, m. p. 38° and 69—70° (*chloroplatinate*; *picrate*, m. p. about 170°) (cf. Kipping, A., 1930, 223), are obtained, the same products resulting from reduction of oximinomethyl Et ketone.

II. The following salts of bistetramethylenepyrazine (I) have been prepared: *hydrochloride* (+H₂O); *hydrobromide* (+3H₂O); *hydriodide* (+3H₂O); *sulphate* (+2H₂O); *oxalate*; *tartrate*, decomp. 190°; *citrate*, decomp. 200°; *benzoate*, decomp. 190°; *salicylate*; *chloroaurate* (+3H₂O); *mercurichloride*; and *chlorostannate*. Reduction of (I) with Na and EtOH gives *bistetramethylenepiperazine*, m. p. 132—133°, also obtained by hydrogenation in presence of Al-Hg and of Ni, but with Pt two stereoisomeric *piperazines*, m. p. 105—106° (*dinitroso*-derivative, m. p. 182°), and m. p. 62—63° (*dinitroso*-derivative, m. p. 107°), result. Reduction does not take place with Et₂O

and Na, Sn and HCl, and SnCl₂. It is suggested that isolation of the three isomerides is connected with the multiplanar configuration of the 6-membered rings. F. R. SHAW.

Mechanism of the formation of indigotin in the von Baeyer synthesis. L. TANASESCU and A. GEORGESCU (Bull. Soc. chim., 1932, [iv], 51, 234—240).—Condensation of *o*-NO₂·C₆H₄·CHO with PhAc in presence of Na₃PO₄ gives Ph β-*o*-nitrophenyl-β-hydroxyethyl ketone, (II), m. p. 108—109° [Bz derivative (I), m. p. 152°], also obtained together with Ph *o*-nitrostyryl ketone by using alkali in place of Na₃PO₄ (cf. A., 1902, i, 879). (I) and (II) with Zn and AcOH at 100° give 2-phenylquinoline. (II) with Zn and AcOH at 0° followed by treatment with FeCl₃ gives a *substance*, m. p. 121°, probably *o*-nitrobenzoylacetophenone. The action of light on Me β-*o*-nitrophenyl-β-hydroxyethyl ketone (improved prep.) in pyridine gives a *substance*, m. p. 170°, and in EtOH a *substance*, m. p. 150° (previous softening). Similar results are obtained with the Bz derivative and with (I) and (II), formation of indigotin being observed in some cases. A. A. LEVI.

Preparation of 7:7'-dimethyl- and 5:7:5':7'-tetramethyl-8:8'-diquinoyl. H. P. WARD and M. G. WARING (J. Amer. Chem. Soc., 1932, 54, 1697).—2-Iodo-3-nitrotoluene and Cu give 6:6'-dinitrodi-*o*-tolyl, which is reduced and then converted (Skraup) into 7:7'-dimethyl-8:8'-diquinoyl, m. p. 213—215°. 5:7:5':7'-Tetramethyl-8:8'-diquinoyl is similarly prepared from 4-iodo-5-nitro-*m*-xylene.

C. J. WEST (b).

Reactions of allantoxanic acid and allantoxaidine with alkali hydrogen sulphites. J. BOUGAULT and (MLLE.) PINGUET (Compt. rend., 1932, 194, 979—981).—A mixture of aq. solutions of alkali allantoxanate or allantoxaidine and alkali H sulphite affords an additive product. These products are decomposed by mineral acids and by I, affording allantoxanic acid and allantoxaidine. The following are described: C₄H₂O₄M.MHSO₃·2H₂O and C₃H₃O₂N₃·MHSO₃·H₂O (M=K or Na).

J. L. D'SILVA.

Preparation of dimethylalloxantin. H. BILTZ and P. NACHTWEY (Ber., 1932, 65, [B], 565—567).—Contrary to Büllmann and Mygind (A., 1930, 1193), the method of Biltz (A., 1913, i, 166) is trustworthy for the prep. of dimethylalloxantin from theobromine. Reduction of methylalloxan by SnCl₂-HCl must be effected slowly at 0°. H. WREN.

Chlorophyll. XX. Conversion of chlorin *e* trimethyl ester into deoxypyrophæophorbide. H. FISCHER and H. SIEBEL. **XXI. Conversion of deoxophylloerythrin and phylloerythrin into chloroporphyrin *e*₅; chloroporphyrin *e*₄.** H. FISCHER, J. HECKMAIER, and J. RIEDMAIER (Annalen, 1932, 494, 73—86, 86—100).—XX. Chlorin *e* Me₃ ester (I) boiled with Na₂CO₃ and pyridine for 72 hr. gives 37% of unchanged (I) and 10% of *deoxypyrophæophorbide* (II), m. p. 230° (*oxime*), which appears to be identical with the product similarly formed (much more readily) from phæophorbide *a*. (II) is a (mono) Me ester, is unaffected by Na₂CO₃ and pyridine, is reduced by HI in AcOH at 55° to phyllo-

erythrin, and is oxidised by O_2 and MeOH-KOH in EtOH-pyridine to a chlorin (reduced by HI to rhodoporphyrin). Chlorin e_7 (III) (*Cu* salt) with Na_2CO_3 and pyridine gives much unchanged (III) and a porphyrin similar to chloroporphyrin e_5 . (III) and moist Ag_2O in boiling EtOH afford a salt, $C_{35}H_{36}O_6N_4Ag$ (reduced to porphyrins showing the spectra of chloroporphyrins e_5 and e_6), whilst (I) gives a salt, $C_{37}H_{40}O_6N_4Ag$. Conant and Hyde's method (A., 1930, 225) of decarboxylating methylphæophorbide affords pyrroporphyrin and phylloerythrin and not a pyrrophæophorbide. The phase test with all deoxypyrrophæophorbides is negative. The production, by ring closure, of (II) from (I) is strong evidence for the authors' formula for (I).

XXI. Deoxyphylloerythrin (IV) (and phylloerythrin) with 20% oleum at room temp. for 42 hr. give chloroporphyrin e_5 (formylrhodoporphyrin) (V); after 24 hr., (IV) affords small amounts of (IV) and (V) and phylloporphyrinsulphonic acid. (V) crystallises from Et_2O in two forms [data by STEINMETZ]. Condensation products could not be obtained from chloroporphyrin e_4 Me (*Fe* and *Cu* salts) or Me₂ esters (*Fe* and *Cu* salts) with Et_2CO_3 , $CH(OEt)_3$, HCO_2Et , $Et_2C_2O_4$, $CH_2(CO_2Et)_2$, or $CO(CH_2CO_2Et)_2$ (rhodo- and phyllo-porphyrins are generally formed), or with PhCHO, *p*-NO₂·C₆H₄·CHO, or *p*-NO·C₆H₄·NMe₂ [the production of (V) is determined spectroscopically]. Chloroporphyrin e_4 is oxidised to (V) by short treatment with cold 20% oleum and by O_2 and MeOH-KOH in EtOH-pyridine; its conversion (by ring closure) into phylloerythrin could not be effected.

H. BURTON.

Derivatives of ætioporphyrin I. H. FISCHER and W. NEUMANN (Annalen, 1932, 494, 225—245).—Ætioporphyrin I (I) [*Zn*, m. p. (Pregl block) 343°, *Ni* (+0.5C₅H₅N), m. p. (block) 327°, *Co*, m. p. (block) 337°, *Ag*, and complex *Sn* salts; *K*₂ derivative, formed from (I) and *K* in xylene and dry CO_2 , whereby only 1 atom of H is produced] and Br (20 mol.) in boiling AcOH give a compound, $C_{32}H_{36}N_4Br_8$, converted by dissolution in AcOH-HCO₂H and pptn. with H₂O into a substance, $C_{32}H_{35}O_3N_4Br_8$, and by treatment with COMe₂ into an O-containing compound containing about 2 Br per mol. (I) in AcOH-HCl treated with H₂O₂ at about 40° gives the dihydrochloride (+COMe₂) (II), m. p. (block) 250°, (tube) 290° (not sharp), of tetrachloroætioporphyrin, decomp. 400° (block) without melting. (II) and pyridine at 30° afford dichloroætioporphyrin (III), m. p. 331° (dihydrochloride), whilst at the b. p. (I) is regenerated. Direct chlorination of (I) gives (III); a monochloro-derivative could not be prepared. The conversion of (II) into ætio-xanthoporphyrinogen by PbO₂ indicates that substitution of the β-side-chains does not occur. (I) and an excess of H₂O₂ in AcOH-HCl give a compound, $C_{10}H_{12}O_{10}Cl$. (I) and aq. NaNO₂ in conc. H₂SO₄ below 70° give a dinitronitrosoætioporphyrin, unaffected by H₂O₂ in H₂SO₄ at -5°, and apparently also formed (spectrum) from dihydroxyætioporphyrin (*Cu* salt), aq. NaNO₂, and H₂SO₄.

[By A. TREIBS.] (I) and HNO₃ (*d* 1.4) give a nitroætioporphyrin, m. p. (block) 287° [*Cu* salt, m. p. (block) 325°], also formed with HNO₃ (*d* 1.48) and

carbamide. In another case, using HNO₂-free HNO₃ (*d* 1.48), dinitroætioporphyrins, m. p. 301° (*Cu* salt, m. p. 325°) and 293°, resulted. (I), HNO₃ (*d* 1.48), and NaNO₂ give a trinitroætioporphyrin, m. p. 293° (*Cu* salt, m. p. 316°), spectroscopically identical with the (NO₂)₃-compound previously described (A., 1928, 1382). (I) and NaNO₂ in AcOH-H₂SO₄ afford a nitro-compound, $C_{32}H_{36}O_4N_6$, m. p. 275° (*Cu* salt, m. p. 321°). In the above cases, nitration is probably accompanied by oxidation.

(I) and Et₂O-MgMeI give ætiophyllin, $C_{32}H_{36}N_4Mg(+MeOH)$, m. p. (block) 347—349° (crystallographic data given), which with picric acid in Et₂O affords the dipicrate of (I). The catalytic reduction of (I) and ætiohæmin is investigated; (I) absorbs 6H with colloidal Pt in AcOH+10% HCl at 36°, but under similar conditions, ætiohæmin is not reduced. The *Ag* salts of mesoporphyrin Me₂ ester and protoporphyrin are described.

H. BURTON.

Ring synthesis of porphyrins with substituted and unsaturated side-chains. III. Synthesis of α-5-carbethoxy-2:4-dimethyl-3-pyrrolysuccinic acid. H. FISCHER, P. HARTMANN, and H. J. RIEDL (Annalen, 1932, 494, 246—263).—Et 2:4-dimethylpyrrole-5-carboxylate and acetylenedicarboxylic acid at 110° give 5-carbethoxy-2:4-dimethyl-3-pyrrolymaleic acid, m. p. 257° (decomp.), reduced by 3% Na-Hg and H₂O at 3—5° to the 5-Et ester, m. p. 240° (decomp.), of α-5-carboxy-2:4-dimethyl-3-pyrrolysuccinic acid, m. p. 172—173° (decomp.).

Et 2:4-dimethyl-3-β-dicyanovinylpyrrole-5-carboxylate (A., 1924, i, 543) and aq. KCN in EtOH give (after acidification) the alkali-sol. Et 2:4-dimethyl-3-αββ-tricyanoethylpyrrole-5-carboxylate (I), m. p. 163°, hydrolysed by 1% NaOH (about 3 mols.) to 3-formyl-2:4-dimethylpyrrole-5-carboxylic acid (II) and by EtOH-HCl to a 5-carbethoxy-2:4-dimethyl-3-pyrrolysuccinic acid mononitrile, m. p. 185° (Me ester, m. p. 166°). (I) and Br in boiling MeOH afford Et 2:4-dimethyl-3-αββ-tricyanovinylpyrrole-5-carboxylate, m. p. 194°. Me(2) Et(5) 4-methyl-3-ββ-dicyanovinylpyrrole-2:5-dicarboxylate and KCN similarly give the 3-αββ-tricyanoethyl derivative, m. p. 167°, hydrolysed by 66% NaOH to 3-formyl-4-methylpyrrole-2:5-dicarboxylic acid, decomp. 260°. Et 2:4-dimethyl-3-β-cyano-β-carbethoxyvinylpyrrole-5-carboxylate and KCN afford Et 2:4-dimethyl-3-αβ-dicyano-β-carbethoxyethylpyrrole-5-carboxylate, m. p. 108°, hydrolysed by EtOH-HCl to the 3-α(or β)-cyano-β(or α)-carboxy-β-carbethoxyethyl derivative, m. p. 183°, by 1% NaOH to (II), and by EtOH-KOH to 2:4-dimethyl-3-β-cyano-β-carboxyvinylpyrrole-5-carboxylic acid, m. p. 240°, or its 5-Et ester, m. p. 241°, according to the amount of KOH used. Et 3-formyl-2:4-dimethylpyrrole-5-carboxylate (III) does not react with CH₂(CO₂H)₂ in EtOH-NH₂Ph; the anil, m. p. 138°, of (III) (converted by KCN into Et 2:4-dimethyl-3-anilinocyanomethylpyrrole-5-carboxylate, m. p. 133°) is produced. 2:4-Dimethyl-3-ββ-dicyanovinylpyrrole and KCN give 2:4-dimethyl-3-αββ-tricyanoethylpyrrole, m. p. 188°; 2:4-dimethyl-3-β-cyano-β-carbethoxyvinylpyrrole-5-carboxylic acid similarly affords the 3-αβ-dicyano-β-carbethoxyethyl derivative, m. p. 180°, hydrolysed (alkali) to (II). 2:4-Dimethyl-3-ββ-

dicyanovinylpyrrole-5-carboxylic acid, m. p. 204°, is obtained from (II) and $\text{CH}_2(\text{CN})_2$ in $\text{EtOH-NH}_2\text{Et}$ at 65°. Et 2 : 4-dimethyl-3- α -dicarbethoxyethylpyrrole-5-carboxylate and carbamide in EtOH-NaOEt at 105—110° give (5-carbethoxy-2 : 4-dimethyl-3-pyrrolyl)methylbarbituric acid, m. p. 240°; with EtOH-NH_3 at 130°, a monoamide, m. p. 191°, results.

Carboxyhæmatic acid, obtained by oxidation of isouroporphyrin II with CrO_3 in dil. H_2SO_4 , has m. p. 154° (decomp.) (cf. A., 1927, 1088), and is identical with the "natural" acid. H. BURTON.

Constitution of bile pigments. VII. "Ætiomesobilirubin" and the nature of the Gmelin reaction. H. FISCHER and E. ADLER (Z. physiol. Chem., 1932, 206, 187—200; cf. A., 1931, 1420).—5-Bromo-4 : 3' : 5'-trimethyl-3 : 4'-diethylpyrromethene hydrobromide when heated with KOAc in AcOH yields 5-hydroxy-4 : 3' : 5'-trimethyl-3 : 4'-diethylpyrromethene (I). Treatment of (I) with $\text{CH}_2\text{Br-CO}_2\text{H}$ equiv. to 2 mols. of Br gives a mixture of hydrobromides from which there were isolated: *product A*, $\text{C}_{31}\text{H}_{36}\text{O}_3\text{N}_4$, dark violet plates, Gmelin reaction negative, but gives blue colour; *product B*, $\text{C}_{31}\text{H}_{38}\text{O}_2\text{N}_4$, emerald-green needles, m. p. 263—265°, Gmelin reaction positive; *product C*, $\text{C}_{31}\text{H}_{38}\text{O}_2\text{N}_4$, bluish-violet prisms, m. p. 253° [*trihydrobromide* (II), violet plates, Gmelin reaction positive, $\text{Zn}(\text{OAc})_2$ reaction positive]. Reduction of (II) with Zn dust in AcOH gives *ætiomesobilirubin*, $\text{C}_{31}\text{H}_{40}\text{O}_2\text{N}_4$, Gmelin reaction as for mesobilirubin. If the Gmelin reaction with mesobilirubin is interrupted at the blue phase the CHCl_3 solution gives the same $\text{Zn}(\text{OAc})_2$ reaction as (II). Condensation of neobilirubic acid with *p*-nitrobenzaldehyde in 25% aq. HCl affords *p*-nitrobenzylideneneobilirubic acid, m. p. 252° (corr.), with *p*-dimethylaminobenzaldehyde, *p*-dimethylaminobenzylideneneobilirubic acid, m. p. 232°, positive Gmelin reaction. The pigments isolated probably correspond with the various colour phases of the Gmelin reaction.

A bilirubin prep. from liver echinococcus on analysis gave figures corresponding with the C_{33} bilirubin formula. J. H. BIRKINSHAW.

Bile pigments. XI. Ferro- and glauco-bilin. H. FISCHER, H. BAUMGARTNER, and R. HESS (Z. physiol. Chem., 1932, 206, 201—210; cf. A., 1931, 497).—Mesobilirubin with FeCl_3 in hot AcOH gives *ferrobilin* (I), $\text{C}_{33}\text{H}_{38}\text{O}_6\text{N}_4\text{FeCl}_3\text{HCl}$, m. p. 260° (decomp.) [Me_2 ester (II), m. p. 255° and m. p. 244°]. With NaOH (I) gives *glauco-bilin* (*dehydromesobilirubin*) (III), sinters at 205—220°, m. p. 304° (decomp.) [Me_2 ester (IV), violet, m. p. 216°, or blue, m. p. 222°]. With aq. Na_2CO_3 , (II) yields (IV). FeCl_3 reconverts (III) into (I), (IV) into (II). In a sealed tube at 215° for 5 min. (III) gives mesobilirubin. Reduction of (III) or (I) with Na-Hg gives mesobilirubinogen. Reduction of (III) with Zn dust in MeOH affords a substance, $\text{C}_{33}\text{H}_{40}\text{O}_6\text{N}_4\cdot 0\cdot 5\text{CHCl}_3$ (from CHCl_3), blackening at 230—240°, m. p. 280° (decomp.). Heating mesobilirubin for 6 hr. in conc. H_2SO_4 at 100° or in boiling HCO_2H gives (III). Neoxanthobilirubic acid in boiling HCO_2H also gives (III). A second *ferrobilin*(?), $\text{C}_{37}\text{H}_{46}\text{O}_6\text{N}_4\text{FeBr}_3\text{HBr}$, m. p.

228°, is obtained from mesobilirubin by the action of HBr and FeBr_3 in HCO_2H . J. H. BIRKINSHAW.

Uteroverdin, the green pigment of the dog's placenta. R. LEMBERG and J. BARCROFT (Proc. Roy. Soc., 1932, B, 110, 362—372).—*Uteroverdin hydrochloride*, the extraction of which is described, in abs. MeOH-HCl gave the *Me* ester, $\text{C}_{35}\text{H}_{38-42}\text{O}_6\text{N}_4$, m. p. 199° (corr., decomp.), which contains 2OMe and is not identical (optical examination) with the *Me* ester of oocyan (A., 1931, 1066). The two pigments, however, give a similar Gmelin reaction and show similar absorption (acid and neutral solution). Uteroverdin, $\text{C}_{33}\text{H}_{34-38}\text{O}_6\text{N}_4$, is provisionally given a structural formula based on that for bilirubin (*ibid.*, 1420).

F. O. HOWITT.

Constitution of cytochrome. K. ZEILE (Z. physiol. Chem., 1932, 207, 35—47).—Repeated reduction and oxidation of hæmin or amorphous hæmatohæmin in pyridine with $\text{Na}_2\text{S}_2\text{O}_4$ and $\text{K}_3\text{Fe}(\text{CN})_6$, respectively, gives a hæmin insol. in pyridine, sol. in neutral and slightly acid aq. media. It resembles cytochrome, but differs in that the porphyrin obtained by elimination of Fe is insol. in Et_2O . Treatment of the product obtained by the action of HBr-AcOH on natural hæmin with glycine *Me* ester gives a complex, $\text{C}_{40}\text{H}_{48}\text{O}_8\text{N}_6$, m. p. 164° (corr.), similar in spectroscopic properties and solubility to cytochrome C and its corresponding porphyrin. It could not, however, be converted into an Et_2O -sol. porphyrin with HBr-AcOH.

J. H. BIRKINSHAW.

Interaction of ammonium and alkylammonium sulphides with aqueous formaldehyde. (MRS.) C. G. LE FÈVRE and R. J. W. LE FÈVRE (J.C.S., 1932, 1142—1148).—Aq. NH_2Me , saturated with H_2S , gives with aq. CH_2O a mixture of a substance (I), $\text{C}_2\text{H}_7\text{NS}$, m. p. 138—139°, and methylthioformaldin (II), (I) being converted into (II) by aq. COMe_2 . NH_2Et , H_2S , and CH_2O form a substance isolated as the hydrochloride, $\text{C}_4\text{H}_9\text{NS}\cdot\text{HCl}$, m. p. 100—150°; piperidine gives a compound, $\text{C}_{12}\text{H}_{26}\text{ON}_2\text{S}$, m. p. 56°; $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ yields a compound, m. p. 248—250° (decomp.), whilst the substances formed from NHMe_2 , NHEt_2 , and NH_2Ph cannot be characterised and are hydrolysed to thioformaldehyde. The action of aq. CH_2O on $(\text{NH}_2)_2\text{S}$ results in a compound, m. p. 200°

$$\begin{array}{c} \text{CH}_2\text{S-CH}_2 \\ | \\ \text{N-CH}_2\text{-N} \\ | \\ \text{CH}_2\text{S-CH}_2 \end{array} \quad (\text{III})$$

(cf. A., 1931, 573), which is probably and a scheme for its formation is suggested.

F. R. SHAW.

Configuration of ephedrine bases. W. LEITHE (Ber., 1932, 65, [B], 660—666).—The configuration of one of the centres of asymmetry of ephedrine is correlated with that of mandelic acid, whereas that of the other is brought into relationship with phenylalanine. l-(+)-Mandelamide is converted by MgMeI into acetylphenylcarbinol, the oxime of which is reduced to *r*-norephedrine containing a small proportion of (+)-norephedrine [oxalate, m. p. 245° (decomp.), $[\alpha]_D^{25} + 22^\circ$ in 2N-HCl; hydrochloride, m. p. 165—170°, $[\alpha]_D^{25} + 30^\circ$]. *dl*- α -Benzylethylamine, b. p. 204°, prepared by reduction of $\text{CH}_2\text{Ph Me}$ ketoxime with Na in abs. EtOH, is resolved by *d*-tartaric acid

in EtOH giving (+)- α -benzylethylamine (I), d^{25}_D 0.940, $[\alpha]^{25}_D +35.6^\circ$, $[d]^{25}_D +29.9^\circ$, $+37.6^\circ$, $+35.8^\circ$, $+54.3^\circ$, $+36.2^\circ$, $+34.5^\circ$, and $+29.4^\circ$ in Et₂O, C₆H₆, cyclohexane, CCl₄, CHCl₃, EtOH, and MeOH, respectively [*H tartrate*, m. p. 182°, $[\alpha]^{25}_D +20.8^\circ$ in *N*-HCl; *Bz* derivative, m. p. 159—160°, $[\alpha]^{25}_D -17^\circ$, -14.8° , $+67^\circ$, and $+72^\circ$ in C₆H₆, CHCl₃, EtOH, and MeOH, respectively; *hydrochloride* (II), m. p. 156°, $[\alpha]^{25}_D +24.8^\circ$ in H₂O]. Treatment of (II) with MeI and KOH affords (+)-deoxyephedrine, thereby establishing the configurative relationship for all natural ephedrine bases. Attempts to correlate (I) with l(-)- α -phenylethylamine (III) by optical comparison of the bases, their *Bz* derivatives, and hydrochlorides lead to conflicting results, so that it is necessary to eliminate the disturbing influence of the Ph group. Catalytic hydrogenation of (III) affords α -cyclobenzylethylamine, d^{25}_D 0.875, $[\alpha]^{25}_D +3.2^\circ$ (*oxalate*, m. p. 132°; *hydrochloride*, m. p. 242°, $[\alpha]^{25}_D -5.0^\circ$ in H₂O; *Bz* derivative, m. p. 162°, $[\alpha]^{25}_D +16.8^\circ$, $+21.4^\circ$, and $+19.2^\circ$ in CHCl₃, EtOH, and MeOH, respectively). (I) is hydrogenated to α -cyclohexylmethylethylamine, $[\alpha]^{25}_D +8.4^\circ$ (*oxalate*, m. p. 180° (decomp.); *hydrochloride*, m. p. 186°, $[\alpha]^{25}_D -1.8^\circ$ in H₂O; *Bz* derivative, m. p. 108°, $[\alpha]^{25}_D +20.3^\circ$, $+31.8^\circ$, $+39.6^\circ$, and $+40.7^\circ$ in C₆H₆, CHCl₃, MeOH, and EtOH, respectively). (+)-Benzylethylamine is therefore configuratively related to l(-)-phenylethylamine. The same configuration is assigned to its *N*-Me derivative, and since all natural *Ephedra* alkaloids can be referred to this compound the asymmetry centre (IV) occurs

Ph in all. The configuration V applies therefore to natural NH₂-C-H OH-C-H (-)-ephedrine. It appears remarkable that the natural *Ephedra* bases are derived from *d*-phenylalanine instead of from *l*-phenylalanine which has the *l*-configuration proper to natural NH₂-acids. H. WREN.

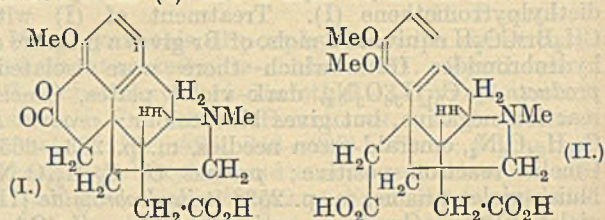
Methylisopelletierine and α -2-*N*-methylpiperidylpropan- β -one. K. HESS and O. LITTMANN (Annalen, 1932, 494, 7—17).—Re-investigation (cf. A., 1919, i, 345; 1925, i, 425) of the synthesis of α -2-*N*-methylpiperidylpropan- β -one (I) (revised data for various derivatives given) confirms Meisenheimer and Mahler's statement (A., 1928, 905) that methylisopelletierine (II) is (I). (II) is only partly demethylated by Diels and Fischer's method (A., 1914, i, 989); the resulting isopelletierine (III) is separable from unchanged (II) by treatment of the mixture with sufficient 2*N*-HCl to neutralise (III) and extraction [of (II)] with Et₂O. Codeine, but not atropine or ψ -pelletierine, can be completely demethylated by Diels and Fischer's method. Edlbacher's method (A., 1918, ii, 336) for the determination of NMe gives vals. of 0.6—0.8% Me with NMe-free substances. Revised data are given for α -2-piperidylpropan- β -one [*i.e.*, (III)] and its derivatives. H. BURTON.

Synthesis and pharmacological action of a homoisopapaverine (and laudanosine). I. Synthesis of 6 : 7-dimethoxy-2-methylquinoline. F. KONEK [with J. DOKTAY] (Math. Nat. Anz. Ungar. Akad. Wiss., 1930, 47, 779—786; Chem. Zentr., 1931, ii, 3485).—6 : 7-Dimethoxy-2-methylquinoline, m. p.

103° [*hydrochloride*, decomp. 220—225°; *chloroplatinate*, $+2H_2O$, m. p. 238—240°; *picrate*, m. p. 218° (decomp.)], was obtained from veratrole by way of nitroveratrole and veratrylamine.

A. A. ELDRIDGE.

Sinomenine. XXX. Sinomenic acid. K. GOTO, K. TAKUBO, and S. MITSUI (Annalen, 1932, 494, 1—6).—Sinomeninone and 30% H₂O₂ in AcOH at 100° give sinomenic acid (I), m. p. 291° (decomp.), $[\alpha]^{25}_D +88.9^\circ$ (all rotations are in H₂O) [*methiodide*, m. p. 239° (softens at 160°), $[\alpha]^{25}_D +61.8^\circ$; *hydrochloride*, m. p. 278—280° (decomp.), $[\alpha]^{25}_D +81^\circ$], which is recovered unchanged when its solution in aq. NH₃ is evaporated. 1-Bromosinomenine is similarly oxidised to 1-bromosinomenic acid, m. p. 251°, $[\alpha]^{25}_D +70.25^\circ$ [*methiodide*, m. p. 276° (decomp.), $[\alpha]^{25}_D +49.7^\circ$; *hydrobromide*, m. p. 306° (decomp.), $[\alpha]^{25}_D +54.82^\circ$; *hydrochloride*, m. p. 292° (decomp.)], also formed from (I) and 1 mol. of Br in hot AcOH.



Methylsinomenic acid (II), m. p. 295° (decomp.), $[\alpha]^{25}_D +12.38^\circ$ (*Ba* salt, decomp. above 300°), and 1-bromosinomenic acid (III), m. p. 261—262° (decomp.) $[\alpha]^{25}_D +34.6^\circ$ (*Ba* salt, decomp. above 300°; *methiodide*, decomp. 249°, $[\alpha]^{25}_D +45.77^\circ$), are obtained by oxidation of methylsinomeninone and the diketone from 1-bromosinomenine (A., 1930, 1049), respectively. The absorption curves of (I), (II), and (III) are similar to that of sinomeninone, which is almost identical with that of sinomenine (IV). (IV) and Br (2 mols.) in EtOH give a perbromide, decomposed by cold Na₂SO₃ to 1-bromosinomenine (70% yield), supporting the view (A., 1931, 1171) that bromination at C₅ is by decomp. of the perbromide.

H. BURTON.

Identification of corynanthine. J. SIVADJIAN (J. Pharm. Chim., 1932, [viii], 15, 352—353).—Corynanthine could not be distinguished from yohimbine by a colour reaction. With either Fröde's, Mandelin's, or Meillère's reagent they give identical colours and also in the (new) reactions with vanillin or piperonal and H₂SO₄ (violet) or with epichlorohydrin and chloranil (brown changing to cherry-red on adding HNO₃).

E. H. SHARPLES.

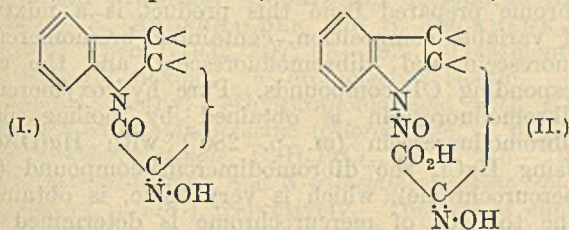
Strychnine and brucine. XIX. Reduction of strychnine methosulphate by means of sodium amalgam in the presence of carbon dioxide. (The late) W. H. PERKIN, jun., R. ROBINSON, and J. C. SMITH (J.C.S., 1932, 1239—1254).—Reduction of strychnine methosulphate by Na—Hg in presence of CO₂ gives tetrahydromethylstrychnine (amorphous) (I), C₂₂H₂₈O₂N₂, cryst. by-products of m. p. 200°.

Strychnine and brucine. XIX. Reduction of strychnine methosulphate by means of sodium amalgam in the presence of carbon dioxide. (The late) W. H. PERKIN, jun., R. ROBINSON, and J. C. SMITH (J.C.S., 1932, 1239—1254).—Reduction of strychnine methosulphate by Na—Hg in presence of CO₂ gives tetrahydromethylstrychnine (amorphous) (I), C₂₂H₂₈O₂N₂, cryst. by-products of m. p. 200°.

m. p. 277°, m. p. 267°, and strychnine. Electrolytic reduction of (I) yields *tetrahydromethylstrychnidine*, b. p. 240—243°/1 mm., and distillation of (I) gives a mixture ($C_{22}H_{26}ON_2$; b. p. 245°/0.3 mm.) of *anhydro-*, m. p. 200—201° (reduced to *di-*, m. p. 160°, and *tetrahydro-*derivatives, m. p. 163—164°), and *demethyleneanhydro-tetrahydromethylstrychnine*, m. p. 172—173° [*methiodide*, m. p. 250—252° (efferv.)]; reduced catalytically to *dihydro-*derivative, m. p. 160—162° (*methiodide*, m. p. about 170°), a further hydrogenation compound being unobtainable pure; and reduced at a Pb cathode to *dihydrodemethylene-tetrahydromethylstrychnidine*, m. p. 98—100°, a *hydrate*, $C_{22}H_{28}O_2N_2$, m. p. 182—184° [*methiodide*, m. p. 250° (decomp.)], a *base*, $C_{22}H_{28}ON_2$, m. p. 217—218° [*methiodide*, m. p. 250° (efferv.)], and a syrup which forms a *methiodide*, m. p. 265—270° (decomp.), a *methochloride*, m. p. 255° (efferv.), and a *methine*, m. p. 70—75°. The constitution of these compounds is discussed.

F. R. SHAW.

New reactions of Strychnos alkaloids. XI. H. WIELAND and W. GÜMLICH (Annalen, 1932, 494, 191—200).—Strychnine and brucine with Et nitrite and EtOH-NaOEt at 40—80° give *oximinostrychnine* (as I), darkens above 200°, not melted at 300°, and *oximinobrucine*, respectively. Dihydrostrychnine similarly affords *oximinodihydrostrychnic acid nitrosoamine* (as II), m. p. about 190° (decomp.); *oximinodihydrobrucic acid nitrosoamine* decomposes at 170° (darkens at 120°). In the prep. of dihydrobrucine hydrate, decomp. 255° (cf. A., 1930, 1455), from



dihydrobrucine (III) and EtOH-KOH, an *isomeride*, m. p. 218°, [α_D^{25} -20.1° in $CHCl_3$ [*methiodide*, m. p. 230° (decomp.)], of (III) is also produced. Brucine and (III) form additive (1:1) *compounds*, decomp. 218—220° and 240—242°, respectively, with $CNBr$ in $CHCl_3$ at 40—50°, which when heated with Zn dust and AcOH regenerate the alkaloids. Tetrahydrostrychnine (IV) and BzCl in pyridine give the *benzoate*, m. p. 172°, of the Bz_2 derivative of (IV), hydrolysed by EtOH-NaOH to the *N-Bz* derivative, m. p. 235°, of (IV). Brucine and maleic anhydride in AcOEt give an additive (1:2) *compound*, decomp. 240°, decomposed by H_2O into its components; (III) affords a similar *compound* (+1.5AcOEt), m. p. 125° (decomp.).

H. BURTON.

Aconitum alkaloids. IX. Molecular formula of oxonitine; oxonine. R. MAJIMA, H. SUGINOME, and H. SHIMANUKI (Ber., 1932, 65, [B], 595—598).—Analyses and determinations of Bz, OMe, and NMe in oxonitine (I), pyroxonitine, and pyroxonine lead to the abandonment of the formula $C_{25}H_{33}ON$ for (I); the results agree more closely with those of Henry (A., 1931, 636) than with those recorded by Späth (*ibid.*, 243). Treatment of (I) with KOH-EtOH

affords *oxonine*, $C_{22}H_{35}O_{10}N_4 \cdot 4H_2O$, m. p. (indef.) 175° after softening at 160°.

H. WREN.

Aconitum alkaloids. X. New Aconitum alkaloid. R. MAJIMA and S. MORIO (Ber., 1932, 65, [B], 599—602; cf. this vol., 178).—Lucidusculine, $C_{24}H_{37}O_4N$ (+1.5 H_2O), decomp. 248—250°, [α_D^{25} -95.5° in $CHCl_3$, yields a *hydrobromide*, decomp. 248—250°, [α_D^{25} -62.7° in H_2O]; *hydrochloride* (+3.5 H_2O), m. p. (hydrated) 98—115°, (anhyd.) decomp. 245—265°; *perchlorate*, decomp. 260—265°, [α_D^{25} -70.3° in EtOH]; *picrate*, m. p. 173—176°; *chloroplatinate*, decomp. 225° after darkening at 217°; and *methiodide*, m. p. 197° after swelling at 187—193°, [α_D^{25} -65.0° in EtOH. Luciculine, m. p. 115—117°, [α_D^{25} -11.4° in EtOH, yields a *hydrochloride* (+1.5 H_2O), decomp. 198—203°, [α_D^{25} -9.4° in H_2O . Acetyl-lucidusculine (*diacetyl-luciduline*) has m. p. 155—157°, [α_D^{25} -76.0° in $CHCl_3$ [*hydrochloride* (+3 H_2O), m. p. 113—117°, anhyd. decomp. 139—144°, [α_D^{25} -50.4° in H_2O .]

H. WREN.

Alkaloids of ergot. A. SOLTYS (Ber., 1932, 65, [B], 553—560).—Ergotinine and ergotamine give analytical data in harmony with the respective formulæ $C_{35}H_{39}O_5N_5$ and $C_{33}H_{35}O_5N_5$ after being dried in air in the dark. Ergotamine, dried in the air, has the composition $C_{33}H_{35}O_5N_5 \cdot 3H_2O$; it loses about 2 H_2O over P_2O_5 at 16 mm. and room temp. and becomes anhyd. over P_2O_5 at 100°/16 mm. The difficulties of analysis are due to unusual hygroscopicity. Ergotoxine does not appear to be a hydrate of ergotinine, but the composition is left undecided. The four alkaloids are sol. in acid and alkali hydroxide and are pptd. by CO_2 from the latter solutions. They do not contain OMe, but 2 NMe groups appear present. With boiling alkali hydroxides they evolve 1 NH_3 , yielding acids the salts of which are not decomposed by CO_2 . The same acid appears to be derived from each alkaloid, but final judgment is hindered by the non-cryst. nature of the acids and their salts. Since the bases evolve β -methylbutyramide when heated, the presence of the group $CHMe_2 \cdot C \cdot CO \cdot NH_2$ is suggested.

Oxidation with $KMnO_4$ and HNO_3 affords BzOH and $p\text{-NO}_2 \cdot C_6H_4 \cdot CO_2H$, respectively. Double linkings do not appear present. 4 active H atoms are detected, one of which is assigned to OH and two to $\cdot CO \cdot NH_2$.

H. FULTON.

Precipitating agents for alkaloids. C. C. FULTON (Amer. J. Pharm., 1932, 104, 244—271).—A review and classification. Suitable concns. are given, and some new reagents suggested. A. A. LEVI.

Organic germanium derivatives. V. Reaction of sodium triphenylgermanide with halogenated methanes in liquid ammonia. C. A. KRAUS and H. S. NUTTING (J. Amer. Chem. Soc., 1932, 54, 1622—1630; cf. A., 1930, 1602).— $NaGePh_3$ and RX in liquid NH_3 give NaX and $GePh_3R$. Thus, MeI gives $GePh_3Me$, m. p. 70.5—71°, which does not react with Na in liquid NH_3 ; EtBr gives $GePh_3Et$, m. p. 78—78.5°, which reacts readily with Br, apparently with the substitution of a Ph group. CH_2Cl_2 gives $GePh_3Me$, $(GePh_3)_2O$, and *ditriphenylgermanylmethane*, $CH_2(GePh_3)_2$, m. p. 134.5°. The last-named compound is the normal reaction product; the other

compounds are formed thus: $2\text{GePh}_3^- + \text{CH}_2\text{Cl}_2 + \text{NH}_3 \rightarrow 2\text{Cl}^- + \text{GePh}_3\text{Me} + \text{GePh}_3\text{NH}_2$ (hydrolysed to the oxide). The same compounds are formed with CHCl_3 as with CH_2Cl_2 but in different proportions. $\text{CH}_2(\text{GePh}_3)_2$ and $(\text{GePh}_3)_2\text{O}$ form solid solutions, separable only with difficulty. The reaction with CCl_4 is similar to but more complex than that with CHCl_3 and CH_2Cl_2 ; free GePh_3 is not formed, but $(\text{GePh}_3)_2\text{O}$ and unidentified compounds are produced. NH_3 probably takes part in the reaction.

C. J. WEST (b).

Arsenical derivatives of thiophen. V. C. FINZI (Gazzetta, 1932, 62, 244—252).—*Thiophen-2-arsenious oxide*, m. p. 115—116°, *5-nitro-*, m. p. 171—172° (decomp.), *5-bromo-*, m. p. 191°, *5-bromo-4-nitro-*, m. p. 245° (decomp.), *5-iodo-*, m. p. 233—234°, and *5-iodo-4-nitro-*, m. p. 157°, *thiophen-2-arsenious oxides*, *di-2:2'-dithienylarsenious oxide*, m. p. 73°, and *di-5:5'-dinitro-2:2'-dithienylarsenious oxide*, m. p. 222°, are prepared by reduction of the corresponding arsenic acids (A., 1926, 186) with SO_2 and a trace of HI. In the prep. of iodothiophenarsinic acid (*loc. cit.*) *di-5-iodo-2-thienylarsinic acid*, m. p. 184° with formation of an anhydride, is also obtained. Nitration of *5-bromothiophen-2-arsinic acid* gives *5-bromo-4-nitrothiophen-2-arsinic acid*, m. p. 288—290°. *5-Bromothiophen-2-arsenious oxide* with MeI and KOH in MeOH gives *methyl-5-bromothiophen-2-arsinic acid* [*2-(5-bromothiophenyl)methylarsinic acid*], m. p. 192°. *5-Nitrothiophen-2-arsinic acid* on reduction with H_3PO_2 followed by heating with excess of S gives *5-nitrothiophen-2-arsenious sesquisulphide*, $(\text{NO}_2\cdot\text{C}_4\text{H}_2\text{S}\cdot\text{As})_2\text{S}_3$, m. p. 60—80°.

E. E. J. MARLER.

Nitroso-derivatives of the phenarsazine series. Action of nitrosyl chloride on derivatives of trivalent arsenic. G. A. RAZUVAYEV and D. A. GODINA [with T. I. JEMELJANOVA] (Ber., 1932, 65, [B], 666—672).—The action of HNO_2 on 10-chloro-5:10-dihydrophenarsazine or phenarsazinic acid does not yield the expected NO-derivative. Addition of HCl to a solution of NaNO_2 and 10-methyl-5:10-dihydrophenarsazine in EtOH affords the *5-nitroso-derivative*, m. p. (indef.) 108—110° without evolution of NO. If NaNO_2 is added to the phenarsazine and HCl, NO is evolved and the formation of the NO-compound is accompanied by that of 10:10-dihydroxy-10-methylphenarsazine (isolated as the oxide), the production of which is not due to direct oxidation by HNO_2 , since 5-acetyl-10-methyl-5:10-dihydrophenarsazine is unaffected by HNO_2 , although readily oxidised by I and H_2O to 10:10-dihydroxy-5-acetyl-10-methyl-5:10-dihydrophenarsazine, m. p. (indef.) 225—240°. *5-Nitroso-10-ethyl-5:10-dihydrophenarsazine* is a viscous liquid; the 10-Ph derivative has m. p. 143—145° (decomp.). In C_6H_6 or EtOH the NO-compounds are rapidly transformed into red, resinous masses owing to partial conversion into NO_2 -compounds and partial oxidation. In presence of HCl the NO_2 -compound is not produced; As becomes quinquivalent and NO is evolved. The NOCl initially formed appears to be added to the As atom with production of 10-chloro-10-nitroso-10-methyl-5:10-dihydrophenarsazine, rapidly hydrolysed to 10-chloro-10-hydroxy-10-methyl-5:10-di-

hydrophenarsazine, m. p. 204°, and thence to the corresponding $(\text{OH})_2$ -compound; the 10-Cl-compound is also derived from NOCl and 10-methyl-9:10-dihydrophenarsazine. AsPh_3 and NOCl in C_6H_6 afford $\text{AsPh}_3\text{Cl}\cdot\text{OH}$. AsPh_3Cl and NOCl in C_6H_6 yield the substance $(\text{Ph}_2\text{AsCl})_2\text{O}$, m. p. 117°, hydrolysed to diphenylarsinic acid. H. WREN.

Mercuration in the aromatic series. VII. Mercury derivatives of *m*-cresol. E. MAMELI and F. PIAGGESI (Gazzetta, 1932, 62, 158—174; cf. A., 1927, 268).—*m*-Cresol with $\text{Hg}(\text{OAc})_2$ under various conditions gives a mixture containing *m-cresol-4-mercuriacetate* (I), m. p. 130°, *m-cresol-6-mercuriacetate* (II), m. p. 155°, *m-cresol-4:6-dimercuriacetate* (III), m. p. 195°, and *m-cresol-2:6-dimercuriacetate* (IV), decomp. at 232—235°. Further mercuration of (I) or (II) gives (III). With benzenediazonium chloride (II) and (III) give 4:6-diphenylazo-*m*-cresol and a compound, m. p. above 210°; (II) also gives 6-benzeneazo-*m*-cresol. By treatment of (I), (II), and (III) with NaCl, NaNO_3 , or Na_2SO_4 *m-cresol-4-mercuri-chloride*, m. p. 209°, *-nitrate*, and *-sulphate*, *-6-mercuri-chloride*, m. p. 212°, *-nitrate*, and *-sulphate*, and *-4:6-dimercuri-chloride*, m. p. 215°, *-nitrate*, and *-sulphate* are obtained, respectively.

E. E. J. MARLER.

Toxicity and chemical constitution of mercurochrome. M. A. PHILLIPS (Quart. J. Pharm., 1932, 5, 1—5).—Bromination of fluorescein in glacial AcOH solution gives dibromofluorescein hydrobromide and unchanged fluorescein. Hence mercurochrome prepared from this product is a mixture of variable composition, containing bromomercurifluorescein and dibromofluorescein, and the corresponding OH-compounds. Pure hydroxymercurodibromofluorescein is obtained by boiling pure dibromofluorescein (m. p. 280°) with $\text{Hg}(\text{OAc})_2$. Using HgCl_2 the dibromodimercuri-compound (dimercurochrome), which is very toxic, is obtained. The toxicity of mercurochrome is determined by the amount of free Hg present. J. B. BATEMAN.

Mercuration of pyridine. N. P. McCLELAND and R. H. WILSON (J.C.S., 1932, 1263—1265).—Mercuration of $\text{C}_5\text{H}_5\text{N}$ and pptn. with brine (cf. Sachs and Eberhartinger, A., 1924, i, 110) affords a mixture containing 3-chloromercuripyridine, m. p. 278—280° (decomp.) and (after treatment with KI) pyridine tri-iodomercuriate, m. p. 152—154° (also prepared from $\text{C}_5\text{H}_5\text{N}$, HI, and HgI_2). F. R. SHAW.

Derivatives of thiodiphenylamine. C. FINZI (Gazzetta, 1932, 62, 175—189; cf. A., 1927, 685).—Alkylation of thiodiphenylamine (I) occurs normally only with MeI and EtI. When heated under pressure with Bu^tI (I) gives *N*-($\alpha\gamma\gamma$ -tetramethylbutyl)thiodiphenylamine, $\text{S} \langle \text{C}_6\text{H}_4 \rangle \text{N}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CMe}_3$, m. p. 209°; with higher alkyl iodides there is no reaction. With PhI, Cu powder, and K_2CO_3 in PhNO_2 (I) gives *N*-phenylthiodiphenylamine (II), m. p. 89—90°, oxidised by KMnO_4 to the corresponding sulphone, m. p. 204—205°; with CH_2PhCl it gives *N*-benzylthiodiphenylamine (III), m. p. 130° (sulphone, m. p. 215—216°). *N*-Methyl- and *N*-ethyl-thiodiphenylamines with $\text{Hg}(\text{OAc})_2$ in boiling EtOH give *N*-methylthiodiphenylamine-2-

mercuriacetate (IV), m. p. 165°, and -2:7-dimercuroacetate (V), decomp. without melting at 290—300°, oxidised by HNO₃ to 2:7-dinitro-*N*-methylthiodiphenylamine sulphoxide (A., 1919, i, 222), and *N*-ethylthiodiphenylamine-2-mercuriacetate (VI), m. p. 153°, and -2:7-dimercuroacetate (VII), decomp. at 300°. With NaCl (IV) gives *N*-methylthiodiphenylamine-2-mercurichloride (VIII), m. p. 234—235°, giving with (I) 2-iodo-*N*-methylthiodiphenylamine, m. p. 107°, and (V) gives *N*-methylthiodiphenylamine-2:7-dimercurichloride (IX), decomp. at 280—290°, giving with Br 2:7-dibromo-*N*-methylthiodiphenylamine, m. p. 198°. With AsCl₃ (VIII) gives *N*-methylthiodiphenylamine-2-arsenious chloride, oxidised by alkaline H₂O₂ to the corresponding *arsinic acid*, m. p. 283° (decomp.), and (IX) gives *N*-methylthiodiphenylamine-2:7-diarsenious chloride, m. p. 195° (acid, decomp. at 230—240°). (II) and (III) do not give mercuriacetates with Hg(OAc)₂ but are oxidised.

E. E. J. MARLER.

Selenobenzaldehyde. L. SZPERL and W. WIORO-GÓRSKI (Rocz. Chem., 1932, 12, 270—275).—Vanino and Schinner's (A., 1915, i, 117) α - and γ -selenobenzaldehydes, m. p. 83—84° and 166°, could not be obtained by their procedure. A *dimeride* of PhCHSe, m. p. 92—93°, and a *trimeride*, m. p. 189—193°, are identified; the latter, which is the chief product of interaction of H₂Se with PhCHO, differs from Vanino's β -selenaldehyde in its lower m. p.

R. TRUSZKOWSKI.

Identification of *l*(+)-isoleucine as component of brain proteins. Separation of leucine mixtures. E. ABDERHALDEN and S. BECKMANN (Z. physiol. Chem., 1932, 207, 93—102).—Treatment of α -bromo-*n*-hexoic, α -bromoisobutylic, and α -bromo- β -methyl- β -ethylpropionic acid with NMe₃ gives *N*-trimethylnorleucine (*chloroaurate*, m. p. 137—138°; *chloroplatinate*, B₂H₂PtCl₆, m. p. 215—216°), *N*-trimethylleucine, and *N*-trimethylisoleucine (*chloroaurate*, m. p. 178°), respectively. The rate of elimination of Br serves to separate norleucine from leucine and isoleucine. The chloroaurates aid identification. The proteins of brain tissue contain *l*(+)-isoleucine.

J. H. BIRKINSHAW.

Optical activity and coagulation of the degradation products of caseinogen. I. B. JIRGENSONS (Biochem. Z., 1932, 246, 219—228).—The optical activity and coagulation of the peptone-like products obtained by degrading caseinogen in glycerol are investigated. From the rotation curve it is concluded that these degradation products have the same configuration as the natural NH₂-acids. Aq. solutions of these products are not coagulated by EtOH, but if the p_H is somewhat increased, coagulation occurs with various alcohols and CMe₂. The degree of pptn. is not proportional to the amount of alcohol, but shows a max. and a min. which differ for the different alcohols.

P. W. CLUTTERBUCK.

Combination curves, hydrogen-ion regulating power, and equivalents of ovalbumin. E. B. R. PRIDEAUX and D. E. WOODS (Proc. Roy. Soc., 1932, B, 110, 353—361).—1.0 and 0.1% aq. solutions of cryst., heat-coagulated, EtOH-denatured, and commercial dried ovalbumin were titrated electrometric-

ally against 0.1*N*-HCl and -NaOH. The solutions of cryst. ovalbumin were dialysed against H₂O and finally against 0.01*N*-AcOH until the NH₃ content was 6 × 10⁻⁶ equiv. per litre. The lack of inflexion on the acid side of the isoelectric point excludes a definition of the acid saturation capacity, the basic groups being progressively opened as the p_H diminishes. Below p_H 3.0 is a slight downward turn peculiar to denatured albumin. Titration on the alkaline side appears to be accompanied by formation of metaprotein: there is no inflexion, and hence ovalbumin, unlike gelatin (A., 1931, 683), shows no sign of saturation with alkali, whilst the buffering power is less const. Ovalbumin, as an acid, has p_{K_A} 3.5 and equiv. 1130 for p_H 2.6—4.4; as an alkali, it has equiv. 1390 for p_H 10.3—11.3 or 10.0—11.6.

F. O. HOWITT.

Metal tube in micro- and semimicro-combustion analysis. S. AVERY, J. BRACKENBURY, and W. D. MACLAY (Ind. Eng. Chem. [Anal.], 1932, 4, 238—239).—The use of Cu combustion tubes with H₂O-jacketed ends is recommended for the micro-determination of C, H, and N. A tube of Ag is recommended for the combustion of compounds containing halogens. A boat-inserter is described.

E. S. HEDGES.

Acidimetric determination of chlorine and bromine in organic substances. II. Semimicro-determination. F. VIEBÖCK (Ber., 1932, 65, [B], 586—588).—The method (this vol., 529) can be applied without modification to semi-micro-practice except that the larger quantities of CO₂ evolved render it desirable to boil the H₂O₂ solution towards the end of the titration.

H. WREN.

Determination of sulphur in organic substances by combustion in an air-stream. F. SEELIG (Angew. Chem., 1932, 45, 281).—A claim for priority (cf. this vol., 291).

E. S. HEDGES.

[Determination of sulphur in organic substances by combustion in an air-stream.] J. SIELISCH and R. SANDKE (Angew. Chem., 1932, 45, 281—282).—A reply to Seelig (cf. preceding abstract).

E. S. HEDGES.

Volumetric sulphate determination. Determination of sulphur in organic compounds. A. CHALMERS and G. W. RIGBY (Ind. Eng. Chem. [Anal.], 1932, 4, 162—164).—The org. substance is oxidised in a Parr S bomb and the SO₄^{''} produced is treated with excess of standard BaCl₂, the excess being determined by aq. Na₂CO₃ and phenolphthalein. Metals which form insol. carbonates must be removed previously, and PO₄^{'''}, AsO₄^{'''}, BO₂['], and CrO₄^{''} interfere.

E. S. HEDGES.

Microanalytical identification of organic substances. V. STANEK and T. NEMES (Z. Zuckerind. Czechoslov., 1932, 56, 390—395).—A micro-method is described in which org. matter is oxidised with iodate in the presence of H₂SO₄, the amount of O thus utilised by many substances agreeing closely with that calc.

J. P. OGILVIE.

Determination of hydrocarbons in air. E. POZNER and R. A. MELIKOVA (J. Appl. Chem., Russia, 1931, 4, 932—939).—Unsaturated hydrocarbons are removed with Pb(OAc)₂, aromatic hydrocarbons with

$\text{H}_2\text{SO}_4 + \text{Ag}$, and naphthenes and paraffins with activated C by passing the air through these reagents in series. The method is applicable to the analysis of low-boiling hydrocarbon mixtures.

CHEMICAL ABSTRACTS.

Colorimetric determination of the vapours of amyl alcohol and amyl acetate in air. I. M. KORENMAN (J. Appl. Chem., Russia, 1931, 4, 940—949).—The vapours are absorbed in EtOH and the filtered solution is treated with furfuraldehyde and H_2SO_4 , the coloration being compared with that of a standard.

CHEMICAL ABSTRACTS.

Determination of acetaldehyde in presence of ethyl alcohol. J. D. PELGROMS (Natuurwetensch. Tijds., 1932, 14, 44—48).—The MeCHO is converted into the HSO_3 compound, the EtOH is determined by the Northrup method, and the MeCHO is determined by decomp. of the HSO_3 compound and titration of the liberated KHSO_3 with I solution. In a method recommended for rapid determinations, HgO is added to one half of the aq. solution, the EtOH is removed by distillation and determined by the $\text{K}_2\text{Cr}_2\text{O}_7$ method; in the other half the total MeCHO + EtOH is determined with $\text{K}_2\text{Cr}_2\text{O}_7$ and the MeCHO is calc. by difference. Practical details are indicated.

H. F. GILLBE.

Refractometric determination of organic acids. (MME.) G. ALLARD (Bull. Soc. chim., 1932, [iv], 51, 372—376).— $\text{H}_2\text{C}_2\text{O}_4$ and $\text{CH}_2(\text{CO}_2\text{H})_2$ (0.0025—0.25N) may be determined by measuring n during pptn. by $\text{Pb}(\text{OAc})_2$. For the individual acids the error is up to 2%; in mixtures, the error in $\text{H}_2\text{C}_2\text{O}_4$ and $\text{CH}_2(\text{CO}_2\text{H})_2$ does not exceed 3% and 6%, respectively.

E. S. HEDGES.

Detection of diacetyl in pyrogenic gases from sugars etc. H. SCHMALFUSS and H. BARTHEMEYER.—See this vol., 592.

Conditions of reduction of Fehling's solution. A. HEIDUSCHKA and W. BIETHAN.—See this vol., 582.

Amino-acid content of ox-horn. Detection of l(+)-norvaline. E. ABDERHALDEN and K. HEYNES.—See this vol., 637.

Improvement in Carobbio's reaction for the detection of traces of resorcinol. L. BEY (Bull. Soc. chim., 1932, [iv], 51, 230—233; cf. A., 1906, ii, 809).— CdSO_4 is 8 times as sensitive as ZnCl_2 and is applicable over wider ranges of concentration.

A. A. LEVI.

Colloidal condition of cholesterol, cholesteryl ester, and lecithin. VI. **Catalytic properties of cholesterol.** I. REMESOV (Biochem. Z., 1932, 246, 431—445; cf. A., 1930, 415).—Provided that O_2 (air) is present, cholesterol (<0.005%) in true or colloidal solution in CHCl_3 gives an immediate emerald-green colour with a mixture of equal vols. of fresh 1% aq. dimethyl-*p*-phenylenediamine and 2:4-diaminotoluene. The intensity of the blue colour, to which the green soon changes, is proportional to the amount of sterol present. The p_{H} should be between 6.2 and 8.2 (optimum at 7.0). Addition of conc. aq. NH_3 causes the CHCl_3 layer to become pink. The reaction is sp. for cholesterol, but impure oleates and lecithin also

give it; with them, however, no pink colour is produced when aq. NH_3 is added. It is probable that a "peroxide" form of cholesterol, which acts as an adsorbed catalyst (analogous to the oxidases), is responsible for the reaction, which consists in dehydrogenation of the amines. Two diamines must be present together in order to satisfy energy requirements. The so-called "oxidones" of Battelli and Stern (A., 1915, i, 346) probably consist of cholesterol. It is possible that there exists, in addition to the biological oxidation system involving Fe, a system involving sterols instead.

W. MCCARTNEY.

Mohler's test for benzoic acid. E. T. ILLING (Analyst, 1932, 57, 224—232).—Grossfeld's modification of Mohler's test has been standardised to give concordant results. The excess of NaOH over BzOH should be as small as possible. Determinations are made on approx. 3 mg. of BzOH. BzOH gives rise to an orange colour, easily distinguishable from the yellow given by salicylic acid or the brown colour of cinnamic acid. When volatile acids sol. in H_2O are present, the BzOH is extracted from the distillate by light petroleum before nitration, and an alkaline oxidation is necessary for distillates from coffee extracts, cordials, and similar products.

T. MCLACHLAN.

[Detection of] novocaine and tutocaine. E. KALLSTRÖM (Svensk farm. Tidskr., 1931, 35, 617—619; Chem. Zentr., 1932, i, 425).—The oil obtained by interaction of tutocaine with HgCl_2 (Rosenthaler, A., 1926, 531) gradually affords crystals which, however, differ in habit from those of the corresponding novocaine compound.

A. A. ELDRIDGE.

Reactions of anæsthesin. L. EKKERT (Pharm. Zentr., 1932, 73, 226—227).—Anæsthesin (0.02—0.03 g.) in H_2O (2 c.c.), treated with HCl (5—10 drops) and then Cl-water gives a white ppt. which on shaking becomes orange-red, sol. in Et_2O or CHCl_3 . The α - and β -naphthol colour reactions show anæsthesin when l in 10^5 . A solution of the hydrochloride gives a red ppt. with 20% bleaching-powder solution.

E. H. SHARPLES.

Microchemical reactions of the furoles. M. WAGENAAR (Pharm. Weekblad, 1932, 69, 449—456).—Several condensation reactions are found suitable for microchemical detection. The most sensitive are those with NH_2Ph and with barbituric acid, by means of which 0.1 mg. may be detected.

S. I. LEVY.

Reactions of arecoline. L. EKKERT (Pharm. Zentr., 1932, 73, 227).—The D.A.B. VI and Rosenthaler's reactions are described. When the hydrobromide is evaporated with H_2O_2 and HCl, the residue dissolved in H_2O and treated with resorcinol and H_2SO_4 , an intense reddish-violet colour is formed which quickly changes to violet and finally to rose. In ultra-violet light it is citron-yellow and on saturation with NH_3 it changes to bluish-violet.

E. H. SHARPLES.

Determination of glutamine in presence of asparagine. A. C. CHIBNALL and R. G. WESTALL.—See this vol., 660.

Determination of amides in presence of carbohydrates. F. BAERTS and P. DELVAUX.—See this vol., 666.

Biochemistry.

Determination of carbon monoxide in blood. J. HERRMANNSEN and H. W. KNIPPING (*Z. physiol. Chem.*, 1932, 206, 168—176).—The gas mixture containing CO is passed over heated I_2O_5 and the liberated I absorbed in aq. KI and determined by titration. The gas stream must be carefully dried and volatile org. substances removed by passage through suitable absorbents. CH_4 and H_2 do not interfere. CO is liberated from blood by $K_3Fe(CN)_6$ and washed out by a neutral gas.

J. H. BIRKINSHAW.

Rate of sinking of red blood-corpuscles. W. M. BENDIEN, J. NEUBERG, and I. SNAPPER (*Biochem. Z.*, 1932, 247, 306—321; cf. *A.*, 1931, 973).—There is not necessarily any connexion between the charge on blood-corpuscles and their rate of sinking. The lability of the proteins of plasma, and, in particular, increases in the amounts of fibrinogen and globulin greatly affect the agglutination and hence the rate of sinking. Small amounts of Na salicylate (but not of NaOBz) stabilise the proteins and hence greatly reduce this rate. Consideration of the factors in the Stokes formula and of the condition of the blood in anæmia lead to the adoption for anæmic blood of a modification of the formula previously given for calculating rate of sinking. True auto-agglutination cannot occur at 30° and is thus distinguished from pseudo-agglutination (van der Hoeden and Verbeek, *Ned. Tijds. Geneesk.*, 1931) which is promoted at this temp.

W. McCARTNEY.

Permeability of vital membranes. The red blood-corpuscle. D. L. WOODHOUSE and F. A. PICKWORTH (*Biochem. J.*, 1932, 26, 309—316).—The permeability of the red corpuscles to various inorg. ions, dyes, and org. compounds of physiological importance is given. 0.4% aq. CH_2O produces no change in the structure of the corpuscles or in the relative permeabilities to bromide and sulphate, nor does 0.5% saponin solution affect the permeability of bromide or sulphate. Veronal and streptococcus toxin in the concns. used also produced no appreciable changes on the permeability. Egg-white as well as the lipid envelope exerts a selective permeability to salts.

S. S. ZILVA.

Non-protein-sulphur content of blood-corpuscles. N. HAJDU (*Z. physiol. Chem.*, 1932, 206, 217—224).—A part of the non-protein-S of the blood-corpuscles is diffusible and part non-diffusible. The concn. of the non-diffusible portion is 4.85—5.25 mg. per 100 c.c. of blood. The diffusible S of the corpuscles is 55% of the plasma-S concn. An equation is derived for calculation of the non-diffusible corpuscular-S from whole blood-S and plasma-S.

J. H. BIRKINSHAW.

Polycythæmia in the rat on a milk-iron-copper diet supplemented by cobalt. J. M. ORTEN, F. A. UNDERHILL, E. R. MUGRAGE, and R. C. LEWIS (*J. Biol. Chem.*, 1932, 96, 11—16).—Rats fed on a milk-Fe diet supplemented by Cu and Co (0.5 mg. as $CoSO_4$ or $CoCl_2$ per day) develop a marked increase

in red blood-cells and hæmoglobin with no change in the leucocyte or differential leucocyte counts.

F. O. HOWITT.

Lectures on blood-sugar. S. L. BHATIA (*Mysore Univ. J.*, 1931, 5, 1—99).

Blood-sugar in abnormal mental states. P. K. McCOWAN and J. H. QUASTEL (*Lancet*, 1931, 221, 731—736).—The hyperglycæmic index has been defined so as to give a quant. expression of the amount of hyperglycæmia sustained after 2 hr., the time required for the blood-sugar level to return to normal in the ordinary way. Sugar tolerance curves are discussed on this basis for 85 psychotic cases. In cases of benign stupor and mania the index is generally low. Arteriosclerosis is not a cause of a high index. During menstruation normal and psychotic cases both show a departure from the normal sugar tolerance curve.

L. S. THEOBALD.

Absence of abnormal forms of glucose from blood dialysates. D. J. BELL (*Biochem. J.*, 1932, 26, 349—352).—The apparent low optical activities of the dialysates may be accounted for by the presence of the levorotatory Na *d*-lactate without assuming the presence of any γ -glucose.

S. S. ZILVA.

Occurrence of thiocyanic acid in blood in normal and pathological conditions, particularly in renal insufficiency; thiocyanic acid-decomposing power of blood. E. BECHER [with K. HAMANN and F. DOENECKE] (*Münch. med. Woch.*, 1932, 79, 1—6; *Chem. Zentr.*, 1932, i, 831).—The CNS' content of the serum and plasma is smaller than that of whole blood; the erythrocytes contain large quantities. In renal insufficiency, particularly in uræmia, the amount rises to 3—5 times the normal. The red corpuscles can decompose CNS-compounds. In the deproteinisation of blood by $CCl_3 \cdot CO_2H$ decomp. of CNS' to H_2S occurs.

A. A. ELDRIDGE.

Bile salts. I. Are there any bile salts in normal blood? S. TASHIRO. II. Pettenkofer reaction of different bile salts and of blood filtrates. S. TASHIRO, E. B. TIETZ, and U. TANGE. III. Pettenkofer reaction of lipins and of blood filtrates. S. TASHIRO, L. H. SCHMIDT, and E. B. TIETZ. IV. Reciprocal relationship between blood-sugar and Pettenkofer-positive substances in mercury poisoning. E. B. TIETZ and S. GOLDBLATT. V. Reciprocal relationship between blood-sugar and Pettenkofer-positive substances in blood during intestinal obstruction. S. TASHIRO and L. H. SCHMIDT. VI. Antagonistic action of glycerol towards bile salts in blood coagulation. S. TASHIRO and O. P. LEE. VII. Antagonistic action of cholesterol to bile salts in blood coagulation. S. TASHIRO and C. A. MILLS. VIII. Antagonistic power of glycerol and cholesterol to bile salts in gastric ulcer formation. S. TASHIRO and S. OLIVER. IX. Antagonistic action of sugars to bile salts in blood coagulation. J. J. KOBES. X. Antagonistic action of

lipins to bile salts in gastric ulcer formation. T. TSURUTA. XI. Antagonistic action of various lipins to bile salts on frog muscles. T. TSURUTA. XII. Antagonistic action of lipins to the toxic action of bile salts. T. TSURUTA. XIII. Antagonistic action of cholesteryl oleate to bile salts in gastric ulcer formation. K. ISHII. XIV. Relation of sex to susceptibility to the toxicity of bile salts. T. TSURUTA. XV. Relation of thyroid activity to the production of gastric ulcer by bile salts. S. TASHIRO and L. H. SCHMIDT. XVI. Relation of blood-phospholipins to experimental gastric ulcer. S. TASHIRO and L. H. SCHMIDT. XVII. Effect of administration of bile salts on Pettenkofer-positive substances and blood-lipin-phosphorus. S. TASHIRO and L. H. SCHMIDT. XVIII. Eczema, an expression of hepatic insufficiency and its cure with bile salt. W. B. WHERRY and S. TASHIRO (Med. Bull. Univ. Cincinnati, 1931, 6, 40—50, 51—61, 62—73, 74—83, 84—89, 90—97, 98—99, 100—101, 102—109, 110—116, 117—123, 124—129, 130—133, 134—136, 137—143, 144—150, 151—155, 156).—I. Normal blood contains slightly $>0.1\%$ of compounds sol. in abs. EtOH or in EtOH+COMe₂ (1:1) and giving a strong Pettenkofer reaction; the substances, which are determined colorimetrically, are pptd. by BaCl₂ or Ba(OH)₂ or by Mg salts in slightly alkaline medium. Cholic acid appears to be absent.

II. The application of the colorimetric method to cholic acid, deoxycholic acid, and mixtures with "blood salts" was studied. The method of determination of Pettenkofer-positive substances in blood can be applied to pure bile salts. When a bile salt is added to the EtOH+COMe₂ extract of plasma the resulting colour val. is less than the sum of the separate colour vals.; apparently a lipid substance renders some of the pigment insol. It is not proved that blood contains deoxycholic acid.

III. The Pettenkofer reactions of lecithin and cephalin are similar to those of deoxycholic acid and "blood salts"; the colours are intensified when the substances are added to blood filtrate. Cholesteryl oleate has the reverse effect. The ultra-violet fluorescence (3660 Å. used) of "blood salts" and of deoxycholic acid is purplish, that of cholic acid being reddish-purple. Normal horse blood contains $<0.0027\%$ of cholic acid, if any.

IV. Increase in blood-sugar was reduced, and the "blood salt" was increased from sub- to super-normal, by intravenous injection of HgCl₂ into cholecystotomised dogs with resected common bile duct.

V. In dogs with operative salivary, œsophageal, or intestinal obstruction nearly all fluctuations in blood-sugar were accompanied by reverse changes in "blood salts" content of the blood.

VI. Delay in clotting caused by Na taurocholate in small quantity is checked by glycerol.

VII. Cholesterol counteracts delay in clotting caused by bile salts.

VIII. Neither glycerol nor cholesterol counteracts.

IX. Glucose, maltose, fructose, rhamnose, and arabinose (in that order of diminishing effect), but not sucrose, antagonise the delay in coagulation

time of citrated horse plasma on recalcification caused by Na taurocholate.

X. Lecithin or crude brain phosphatide counteracted the effect of Na glycocholate.

XI. Crude phosphatide mixture, lecithin, sulpholipin, and cephalin (in that order of diminishing effect) antagonise the tetanic effect of bile salts.

XII. The toxic effects of cholic and deoxycholic acids on frogs and guinea-pigs are compared. Glucose, olive oil, and phosphates have no antagonistic effect.

XIII. Cholesteryl oleate antagonises the action of bile salts.

XV. Feeding thyroxine lowers the ulcer-producing dose of bile salt in guinea-pigs, possibly by reduction of the phospholipins as a result of increased general lipin metabolism.

XVI. Changes in (rabbits') blood-phospholipins on treatment with gastric ulcer-producing agents are recorded; a decrease occurs in all the treatments.

XVII. Oral administration of Na taurocholate and glycocholate (0.1—0.2 g. per day for 14 days) to normal and pathological human subjects resulted in the "blood salts" becoming more nearly normal; in all normal cases the lipin-P decreased.

CHEMICAL ABSTRACTS.

Determination of ergothioneine in blood-filtrates. J. A. BEHRE (Biochem. J., 1932, 26, 458—460).—Salt's results (A., 1931, 1440) are criticised.

S. S. ZILVA.

Photochemical degradation of hæmoglobin and its reaction-relationship to chlorophyll. G. KÖGEL (Strahlenther., 1931, 42, 379—383; Chem. Zentr., 1932, i, 533).—Chlorophyll is decomposed by light more rapidly in presence than in absence of quinones. Hæmoglobin is decomposed to complete decolorisation in presence of hæmatin or K glucothiose.

A. A. ELDRIDGE.

Blood-glutathione. V. SCHELLING (J. Biol. Chem., 1932, 96, 17—24).—The reduced glutathione in the blood as determined by Mason's method (A., 1930, 803) averages 0.0213% in males and 0.0227% in females. Arterial and venous bloods differ in the amount of SH-groups. The SH-content is decreased on aëration and entirely destroyed by H₂O₂. Reduction of Folin-Wu blood filtrates by nascent H increases the SH-content, whereas there is no such increase if the filtrate has been previously oxidised by H₂O₂. Hence substances other than oxidised glutathione are reduced by nascent H and are determined in the method used.

F. O. HOWITT.

Physico-chemical differences between α -, β -, and γ -hæmoglobins. II. T. TADOKORO, M. ABE, and K. YOSHIMURA (J. Biochem. Japan, 1932, 15, 197—204).—Horse oxyhæmoglobin was separated into three fractions by differences in solubility in H₂O. The globins from these three fractions differed in isoelectric point, sp. rotation, and distribution of the constituent NH₂-acids (cf. this vol., 292).

F. O. HOWITT.

Denatured globin. N. U. MELDRUM (Biochem. J., 1932, 26, 162—164).—Meldrum and Dixon's observation (A., 1930, 803) that denatured globin gives no nitroprusside test for SH or S-S groups is confirmed. The colour reaction observed by Anson

and Mirsky (A., 1931, 972) is due to COMe_2 used in the prep. of globin. A. COHEN.

Amide-nitrogen in the blood of children. A. BERNHARD and J. S. LEOPOLD (Amer. J. Dis. Children, 1931, 42, 1100—1102).—The val. (98—132 mg. per 100 c.c.) appears to be independent of the lactic acid concn. and CO_2 -combining power of the blood. CHEMICAL ABSTRACTS.

Amide-nitrogen of blood. VI. S. BLISS (J. Pharm. Exp. Ther., 1932, 44, 397—407; cf. A., 1931, 110).—A reply to Nash and Williams (this vol., 295). H. DAVSON.

Determination of residual nitrogen in blood. L. N. LAPIN and W. E. KILL (Z. klin. Med., 1931, 148, 278—285; Chem Zentr., 1932, i, 261).—The blood is deproteinised with ZnSO_4 and NaOH , ashed by Kjeldahl's method, and treated with Nessler's and Fehling's reagents, when a green colour appears. The colour is compared with that similarly obtained from NH_4Cl . A. A. ELDRIDGE.

Residual nitrogen and its determination. Y. JÄDERHOLM (Erip. Aikakaus. Duodecim, 1930, 417—434; Chem. Zentr., 1932, i, 261).—A discussion. A. A. ELDRIDGE.

Changes in blood-chlorine and -water with oxygen-deficient air. D. ADLERSBERG and J. GLASS (Arch. exp. Path. Pharm., 1932, 165, 383—400).—Fasting rabbits exposed for 72 hr. to air at a pressure equiv. to that at a height of 6000 m. experience a decrease in the alkali reserve of the blood, an increase of plasma-Cl, and a decrease of plasma- H_2O . The corpuscles show irregular variations in Cl content and, on the average, an increase in H_2O , the val. of the ratio corpuscular-Cl/corpuscular- H_2O : plasma-Cl/plasma- H_2O decreasing in each instance. Control fasting animals show an increase in this ratio. The changes due to deficiency of O_2 are, to a certain degree, similar to those occurring with decrease of CO_2 tension of blood *in vitro* or with hyperventilation alkalosis *in vivo*. F. O. HOWITT.

Iodometric determination of iron in blood. J. H. BLACKWOOD and J. D. STIRLING (Biochem. J., 1932, 26, 353—356).—The method is based on the liberation of I from KI by Fe^{+++} at $[\text{H}^+]$ on the acid side of neutrality, when the reaction is quant. Results accurate to about 2% are obtained with 2 c.c. of blood. S. S. ZILVA.

Application of Winterstein's micro-electrode to determination of blood- p_{H} . W. LAUBENDER (Arch. exp. Path. Pharm., 1932, 165, 1—4).—The Winterstein micro-electrode cannot in general be applied for the determination of the p_{H} of blood because of the uncontrollable loss of CO_2 . W. O. KERMACK.

Effect of bile acids on the hydrogen-ion concentration of the blood. T. IROO (Arb. Med. Univ. Okayama, 1931, 2, 572—578).—Injection of bile salts increases the alkali reserve of dog's blood but does not affect the p_{H} . Removal of bile from the gall-bladder diminishes the p_{H} and alkali reserve; injection of bile acids produces normal or supernormal vals. CHEMICAL ABSTRACTS.

Variations of serum-calcium in the rabbit. M. C. BOURNE and D. A. CAMPBELL (Biochem. J., 1932, 26, 183—195).—The wide variation of serum-Ca in normal rabbits is decreased by fasting. A cabbage diet results in increased serum-Ca (14.3—19.3 mg. per 100 c.c.), decreased inorg. serum-P, and a large vol. of alkaline urine rich in Ca, poor in P. Oats cause decreased serum-Ca (11—15.8 mg. per 100 c.c.), increased serum-P, and a small vol. of acid urine rich in P, poor in Ca. A. COHEN.

Osmotic behaviour of the water of blood-serum. F. W. SUNDERMAN (J. Biol. Chem., 1932, 96, 271—283).—The addition of sucrose (0.06—0.98M) to NaCl solutions and to serum, and the addition of NaCl to serum, all produce the theoretical f.-p. depression, calc. on the basis of total H_2O ; the effects of urea on serum and on solutions of NaCl and sucrose are slightly less than theoretical. It is concluded that the total H_2O of serum is osmotically "free." J. B. BATEMAN.

Physical method for following changes produced in serum by dilution. A. BOUTARIC and M. DOLADILHE (Compt. rend., 1932, 194, 1385—1387).—To characterise the behaviour of serum diluted with distilled H_2O the following magnitudes are important: (1) the degree of dilution, L , at which the pptn. is a max.; (2) the val. at this dilution of the product LH (where H is the optical density). W. O. KERMACK.

[Determination of serum-]alkali reserve. J. MÜLLER (Klin. Woch., 1931, 10, 2038—2040; Chem. Zentr., 1932, i, 262).—Ellinger's method (*ibid.*, 1931, 10, 2036) is acceptable, but not the expression of the results in vol.-% of CO_2 . The method is inapplicable to hæmolytic, icteric, turbid, or lipæmic sera. A. A. ELDRIDGE.

Diffusible and non-diffusible serum-calcium following intravenous injection of calcium salts. R. G. SMITH and H. R. STERNBERGER (J. Biol. Chem., 1932, 96, 245—257).—When serum-Ca of dogs is increased by intravenous injection of Ca chloride, lactate, or gluconate, both diffusible and non-diffusible parts in the serum rise, so that the normal relation is approx. maintained. This is not explainable by a rise in serum-protein or by exchange between blood and tissues, since the same result is obtained *in vitro*. Diffusible Ca tends to be adsorbed on collodion sacs during ultrafiltration. J. B. BATEMAN.

Mineral constituents of the blood-serum and survival of tissue from *Vipera aspis*. P. DODEL and P. FEBURE (Bull. Soc. Chim. biol., 1932, 14, 272—274).—The blood-serum of *V. aspis* contains Na 3.9, K 0.30, Ca 0.19, glucose 0.1 g. per litre. The striated muscle survived for 50 hr. in a solution containing NaCl 8.4, KCl 0.5, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ 0.68, glucose 0.5, NaHCO_3 1 g. per litre, and smooth muscle for 7—8 hr. in a solution containing NaCl 9, KCl 0.5, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ 0.67, glucose 0.5, MgCl_2 0.01, NaHCO_3 0.5 g. per litre of H_2O . The addition of 3 c.c. of human blood-serum to 250 c.c. of the second solution prolonged the survival of the muscle. A. LAWSON.

Refractometric investigation of serum-proteins. IX. Ultrafiltration of serum under high

pressure. D. VON DESEÖ and E. LAMOTH (Biochem. Z., 1932, 247, 322—328; cf. this vol., 412).—When horse-serum is subjected to fractional ultrafiltration under pressure (up to 120 atm.) gradual increase in n of the fractions is observed, the last fraction having the highest n . The amounts of the org. and inorg. constituents of the serum increase to equal extents, since their n does not change during the process. Removal of bound H_2O by the pptd. protein may be the cause of the increase in n of the ultrafiltrates. For the determination of n the first ultrafiltrate only should be used. W. McCARTNEY.

Transformation of serum-albumin into serum-globulins. A. FISCHER (Science, 1932, 75, 443).—Albumin-antiprothrombin compounds behave as globulins and must be regarded as identical with them. The addition of small amounts of antiprothrombin (heparin) results in an increased amount of globulin in the serum. Antiprothrombin is the only substance, normally found in the body, which can form globulins, and the amount of globulins present in blood-serum is determined by the amount of antiprothrombin. L. S. THEOBALD.

Determination of serum-carotene. F. D. WHITE (J. Lab. Clin. Med., 1931, 17, 53—59).—Palmer's method is modified. The normal serum-carotene is 0.063, and diabetic 0.072—0.379, mg. per 100 c.c. CHEMICAL ABSTRACTS.

Specificity and chemical structure. H. BIERRY (Compt. rend., 1932, 194, 1271—1273).—Amongst the carbohydrates present in the products of hydrolysis of the proteins of dog's plasma, galactose, mannose, and glucosamine are identified, the percentage of the last two constituents being much less than in the case of the horse. W. O. KERMAK.

Determination of cholesterol in blood-serum or -plasma. A. BERNHARD and I. J. DREKTER (J. Lab. Clin. Med., 1931, 16, 1225—1229).—Modifications are proposed (cf. A., 1918, ii, 336). A mixture of equal parts of EtOH and Et₂O is the most efficient agent for extracting cholesterol when filter-paper is used as the absorbent. CHEMICAL ABSTRACTS.

Plasma-lipins and stability of blood-suspensions. B. ÖHLSON and O. RUNDQVIST (Biochem. Z., 1932, 247, 249—256).—Removal of the lipins from blood-plasma (without denaturation of the proteins) causes no change in the rate of sinking of red corpuscles in the plasma. The increased stability of normal blood-suspensions produced by heat is not found in the lipin-free plasma. W. McCARTNEY.

Method of immunisation with carbohydrate haptens adsorbed on collodion particles. J. FREUND (Science, 1932, 75, 418).—Rabbits injected with collodion particles coated with the sp. substance from pneumococcus type III did not produce agglutinins or precipitins. A faintly positive precipitin reaction was obtained in the case of 1 out of 3 rabbits injected with anthrax-carbohydrate coated on collodion. L. S. THEOBALD.

Inorganic constituents of cerebrospinal fluid. II. Ultrafiltration of calcium and magnesium from human sera. E. WATCHORN and R. A.

McCANCE (Biochem. J., 1932, 26, 54—64).—The ratios of ultrafiltrable Ca(Mg): total serum-Ca and -Mg are nearly const. in normal and pathological cases, and are 57 and 75%, respectively. In pregnancy total serum-Mg and -Ca tend to fall and the ultrafiltrable fractions to increase. "Parathormone" administration caused a fall in the ultrafiltrable Ca:total serum-Ca ratio. A. COHEN.

Cuprous glutathione. N. W. PIRIE Crystallography of glutathione. J. D. BERNAL (Biochem. J., 1932, 26, 75—79).—The Cu⁺ compound has $[\alpha]_{D}^{16.5}$ +45.1° and +45.4—45.8° when prepared from reduced and oxidised glutathione, respectively. Analytical data do not verify the existence of a Cu⁺ derivative of oxidised glutathione of the type Cu₂GS·SG (Kozlowski, this vol., 77). Crystallographic data for glutathione are given. A. COHEN.

Phosphorus and glutathione contents of the atrioventricular bundle. G. DEL GUERRA (Arch. Ital. Biol., 1931, 85, 182—189; Chem. Zentr., 1931, ii, 2628).—The atrioventricular bundle contains 1% of total P and 0.36% of org. P. The iodometric method gives a glutathione content of 123 mg. per 100 g. of muscle tissue. L. S. THEOBALD.

Chemical nature of unsaponifiable fraction of fish-liver oils. II. Cod-liver oil. G. WEIDEMANN and F. ENDER (Biochem. J., 1932, 26, 264—268).—The unsaponifiable matter of cod-liver oil was treated with phthalic anhydride in C₅H₅N, and the alkyl H phthalates were fractionated. In addition to cholesterol, two dihydric aliphatic alcohols (I vals. 64 and 160), a monohydric cyclic alcohol, m. p. 144°, a dihydric cyclic alcohol, and a hydrocarbon giving an SbCl₃ colour reaction 250 times as intense as that of cod-liver oil were obtained. A. COHEN.

Oil of the moon-fish; modifications due to parasites; abnormal content of cholesterol. H. MARCELET (Compt. rend., 1932, 194, 1392—1393).—The oil extracted from the liver of a "moon fish" (*Orthogoriscus mola*) strongly infested with parasites (*Anthocephalus gigas*) differed from that of a healthy specimen in being less in amount (2.7 g. instead of 31.0 g. per 100 g. of liver) and containing less cholesterol (20.0% instead of 35.5%). W. O. KERMAK.

Swelling of single collagen fibre-bundles. R. H. MARRIOTT (Biochem. J., 1931, 26, 46—53).—A technique for the microscopical measurement of fibre-bundles is described. They are rendered less sensitive to the swelling action of acid by repeated use. The combined effects of "plumping" and "opening out" of the fibres determine the extent of the swelling. This is max. at p_H 1.9 for pure collagen and at p_H 2.8 for fresh ox-hide fibre-bundles which undergo more opening out, a process occurring at higher p_H . A. COHEN.

Phosphatides. IV. Unsaturated fatty acids of the ether-soluble phosphatides of brain. E. KLENK (Z. physiol. Chem., 1932, 206, 25—40; cf. A., 1931, 1321).—Fractions of highly and weakly unsaturated acids were obtained with the aid of the Li salt-COMe₂ and of the Pb salt-EtOH methods. The esters were then further fractionated by distillation. The C₁₃ fraction consisted principally of oleic

acid. The C_{20} group contained an acid, $C_{20}H_{38}O_2$, m. p. 20° , probably identical with gadoleic acid, and an acid, $C_{20}H_{32}O_2$, probably arachidonic acid. The C_{22} fraction contained mainly an acid, $C_{22}H_{40}O_2$, probably clupanodonic and smaller amounts of acids with <5 double linkings. J. H. BIRKINSHAW.

Enzymes in the intestines of *Haliotis giganteus*, Gm. K. OSHIMA (J. Agric. Chem. Soc. Japan, 1931, 7, 328—331).—Cellulase, amylase, gelase, and rennin were present; *alginate* hydrolysed alginic acid from brown seaweeds. Weak reactions for invertase, maltase, and protease were obtained; tyrosinase, amygdalase, and esterase were not found.

CHEMICAL ABSTRACTS.

Presence of an acid-soluble organic phosphorus compound in the submaxillary gland of the dog. A. ROSSI and G. SCOZZI (Atti R. Accad. Lincei, 1931, [vi], 14, 582—585).—The gland contains about 0.14 g. of P per 100 g. of the fresh tissue, about 0.04 g. of this being in the form of an acid-sol. compound. The fact that part at least of the latter is determinable only after incubation at 37° indicates it to be a labile org. P compound the behaviour of which recalls that of phosphagen. T. H. POPE.

Reaction of the thiol group. A. GIROUD and H. BULLIARD (Bull. Soc. Chim. biol., 1932, 14, 278—279).—The presence of the SH group may be shown by treatment of the material with 5% aq. $Zn(OAc)_2$ and washing with H_2O before carrying out the nitroprusside reaction. A lasting red coloration is obtained. Creatinine, $COMe_3$, and substances containing the $\cdot S \cdot S \cdot$ group do not give the reaction.

A. LAWSON.

Total and thyroxine iodine in the thyroid of the horse. L. BLANCHARD and H. SIMONNET (Bull. Soc. Chim. biol., 1932, 14, 229—237).—In nine cases the normal thyroid tissue of the horse contained 0.031—0.177 g. of total I, and 0.009—0.086 g. of thyroxine-I per 100 g. of fresh material. In three cases, the total I was 0.260—0.334 g., and the thyroxine-I 0.128—0.189 g. per 100 g. of dry material. In four cases the fetal thyroid contained 0—0.0133 g. of total I per 100 g. of fresh tissue, and in the one case examined, the foetal thyroid at birth showed the same I content as that of the mother. Putrefaction caused complete disappearance of thyroid-I only when continued for 12 days. The total I and thyroxine-I content of several pathological thyroids were in general below the normal vals.

A. LAWSON.

Amino-acid content of ox-horn. Detection of *l*(+)-norvaline. E. ABDERHALDEN and K. HEYNS (Z. physiol. Chem., 1932, 206, 137—145).—The fraction of the hydrolysis products analysing to aminovaleric acid was converted into the corresponding α -bromovaleric acids with $NOBr$ and these were separated by their different rates of amination. The hydantoins obtained by means of $PhNCO$ were identical with those from *d*(-)-norvaline [*d*(+)-3-phenyl-5-n-propylhydantoin, m. p. 112° , $[\alpha]_D^{20} +73.4^\circ$ (in EtOH)], and *l*(+)-valine [*l*(-)-3-phenyl-5-isopropylhydantoin, m. p. 133° , $[\alpha]_D^{20} -92.3^\circ$ (in EtOH)]. Ox-horn keratin therefore contains *l*(+)-norvaline (Walden inversion on bromination and amination)

and *l*(+)-valine. In addition *l*(-)-histidine and 15% of glutamic acid were detected.

J. H. BIRKINSHAW.

Vital staining of trout eggs. P. ADLER (Proto-plasma, 1932, 15, 15—23).—The capsule of fertile and unfertilised (but surviving) trout eggs is equally permeable to acidic and to basic stains dissolved in 0.8% NaCl solution. The penetration of Congo-red is somewhat limited. Dyes do not enter the interior portion of the egg while the latter is still alive. Injury to the egg by the dye is least when applied in 0.8% (isotonic) NaCl solution. The primary injury is associated with an increased permeability of the surface of contact.

A. G. POLLARD.

Isolation of pure, anhydrous ethyl alcohol from non-alcoholic human and animal tissues. A. O. GETTLER, J. B. NIEDERL, and A. A. BENEDETTI-PICHLER (J. Amer. Chem. Soc., 1932, 54, 1476—1485).—Micro-apparatus for the isolation of pure anhyd. EtOH from extremely dil. solutions (0.0025% or less, as found in tissues) is described. The average quantity of EtOH normally present in body tissues is: human brain, 0.0004%; human liver, 0.00256%; human blood, 0.004%; dog brain, 0.003%; dog liver, 0.0007%; dog blood, 0.0013%; pig brain, 0.00007%.

C. J. WEST (b).

Relationship between sugar in blood and lactic acid in brain. E. G. HOLMES and M. A. F. SHERIF (Biochem. J., 1932, 26, 381—387).—The lactic acid content of mouse brains fixed rapidly in liquid air is invariably low. The amount formed on anaerobic incubation depends on the blood-sugar level at death up to blood-sugar vals. of some 200 mg. per 100 c.c. At higher levels there is a smaller increase in lactic acid in proportion to the increase in blood-sugar which is due to a corresponding failure of the brain tissue to take up carbohydrate. At blood levels at which hypoglycæmic symptoms occur the "resting" brain-lactic acid level is decreased.

S. S. ZILVA.

Amino-acids of tissues. VI. Determination of basic amino-acids in small quantities of proteins. J. L. ROSEDALE and G. A. DA SILVA (Biochem. J., 1931, 26, 369—376).—Separate samples are hydrolysed with acid and with alkali. Histidine is pptd. by $HgSO_4$ from the alkaline hydrolysate. The remaining data obtained from the material yielded by the acid hydrolysis offer information which is ordinarily given by Van Slyke's method. Gelatin, caseinogen, oysters, and *Torula utilis* were analysed by this method and the results are given. Prolonged hydrolysis of proteins with acid is required completely to destroy tryptophan.

S. S. ZILVA.

Amino-acids. V. T. YAGINUMA, G. ARAI, and K. HAYAKAWA (Proc. Imp. Acad. Tokyo, 1932, 8, 91—93).—From 5 kg. of spinal cord from cattle 2 g. of pure cryst. norleucine (m. p. $276-278^\circ$) were isolated. Crystal consts. of formyl-*l*-leucine, m. p. $142-144^\circ$, and of the formyl derivative, m. p. $115-116^\circ$, of the synthesised *d*-norleucine are given.

W. R. ANGUS.

Body-fats of the pig. Formation of animal depôt fats. A. BANKS and T. P. HILDITCH (Biochem. J., 1932, 26, 298—308).—The outer back, inner

back, and leaf fats from pigs receiving fish-meal in their diet were investigated. The different component acids of each of these groups showed a numerical relationship similar to that previously observed (this vol., 189). The united molar percentages of stearic, oleic, and linoleic acids were approx. 70%. The increase in stearic acid was again mainly at the expense of oleic and not of linoleic acid. The relationship between the molar percentage of fully-saturated glycerides and the total molar content of saturated acids was very similar to that observed in the cases of tallows and butter-fat (A., 1931, 757, 1178). Fish-meal diets lead to the production of extremely soft fat due to the general increase in unsaturated components, especially to unusually large proportions of linoleic acid. S. S. ZILVA.

Determination of the hydrogen-ion concentration of the tissues in living animals. C. VOEGTLIN and H. KAHLER (Science, 1932, 75, 362—364).—A method using a capillary glass electrode is described. L. S. THEOBALD.

Formation of ammonia in the kidney. H. WASSERMAYER (Arch. exp. Path. Pharm., 1932, 165, 420—431).—Adenosinephosphoric acid, which occurs in the dog's or rabbit's kidney in amounts equiv. to approx. 10 mg. of NH_3 , serves as a source of NH_3 . Analysis of the efferent and afferent blood-streams of the kidney indicates a synthesis of adeninephosphoric acid. The *post-mortem* liberation of NH_3 from kidney pulp is, however, greater than can be accounted for by the content of the acid. The normal content of NH_3 in the kidney is $< 0.001\%$. To a smaller extent the presence of adenosinephosphoric acid and the formation of NH_3 are also observed in the blood, submaxillary and parotid glands, stomach, spleen, lungs, and liver. F. O. HOWITT.

Adrenal cortex and muscle chemistry. K. LANG (Pflüger's Archiv, 1931, 229, 60—85; Chem. Zentr., 1932, i, 830).—In the muscle of adrenalectomised cats the NH_3 content is double the normal; the phosphagen content falls to 33%. Other values were normal. A. A. ELDRIDGE.

Actual acidity of the hæmolymph of *Bombyx mori*. L. I. Metabolism of silkworms. S. DEMJANOVSKI, R. GALZOVA, and V. ROSHDESTVENSKA (Biochem. Z., 1932, 247, 386—405).—During the caterpillar and pupal stages the hæmolymph of *B. mori* has p_{H} 6.7—6.8. At each of the five sheddings of skin the acidity undergoes considerable reduction. Differences in the acidity occur at various stages of growth (egg to butterfly, winter rest period included) and there are also differences due to sex.

W. McCARTNEY.

Magaki (*Ostrea gigas*, Thumberg). I. Difference in composition according to sex. B. MASUMOTO, M. MASUMOTO, and M. HIBINO (J. Sci. Hiroshima Univ., 1932, 2, 155—158).—The female oysters have a heavier shell and more soft tissue than the male. A similar difference exists in the abs. and % contents of H_2O , total N, fat, and glycogen. F. O. HOWITT.

Effect of diet rich in phosphatides on the phosphatide content of milk. A. TRAUTMANN and H. KIRSCHHOFF (Biochem. Z., 1932, 247, 275—296).—The

phosphatide content of goat's milk is only occasionally and temporarily increased and the composition of the milk is but little affected as a result of administration of lecithin. W. McCARTNEY.

Absorption of milk precursors by the mammary gland. I. Kaufmann-Magne technique. II. Relation of blood-sugar absorption to lactose secretion. J. H. BLACKWOOD and J. D. STIRLING (Biochem. J., 1932, 26, 357—361, 362—368).—I. The corpuscular vol. and the Fe content of the blood from the radial artery and the jugular and abdominal subcutaneous (mammary) veins of lactating and non-lactating cows have been determined. The differences in the contents of indiffusible constituents are alike in lactating and non-lactating animals. The content of the indiffusible constituents of the jugular blood is higher than that of arterial or mammary blood. There therefore appears to be a withdrawal of H_2O from the arterial blood by the salivary glands.

II. In non-lactating cows the sugar content of the jugular blood is lower than that of the mammary venous blood, which is itself lower than that of arterial blood. In lactating animals the sugar content of the jugular blood is higher than that of mammary venous blood, but lower than that of arterial blood. The great lowering of mammary venous blood-sugar in lactating animals is partly due to the increased energy requirements of the active gland and partly to lactose secretion. S. S. ZILVA.

Determination of zinc in milk. M. SATO and K. MURATA (Trans. Tottori Soc. Agric. Sci., 1931, 2, 206—223).—Milk ash is dissolved in 2N-HCl, diluted with H_2O , and heated to boiling; Fe is pptd. with aq. NH_3 and Mn with $(\text{NH}_4)_2\text{S}$. The cold filtrate is acidified with HCl; Na_2CO_3 is added to alkalinity (Me-orange), then 50% HCO_2H to acidity. ZnS is pptd. with H_2S from the boiling solution, the gas being passed until the solution is cool. The ZnS is dissolved in 15% HCl (6 c.c.), Zn being determined nephelometrically as $\text{Zn}_2\text{Fe}(\text{CN})_6$. The Zn content was highest immediately after parturition; it decreased gradually and then slightly increased towards the end of lactation. Human milk contained (average) 7.35, 1.23, and 3.89 mg. per litre 3, 25, and 360 days after parturition, respectively. Cow's milk contained 13.57 mg. immediately after parturition, 2.35—2.12 mg. in the 2nd or 3rd month, and 4.58 mg. at the end of lactation. The average Zn content of market milk was 3.3 mg. Ewe's milk contained 13.78 mg. immediately after parturition, 2.45—2.90 mg. during 1—7 months, and 3.5 mg. at the end of lactation.

CHEMICAL ABSTRACTS.

Peptic degradation of caseinogen. H. HOLTER, K. LINDERSTRØM-LANG, and J. B. FUNDER (Z. physiol. Chem., 1932, 206, 85—115).—Samples of caseinogen obtained by fractionation with HCl in EtOH, also commercial preps., were subjected to peptic digestion, and the hydrolysis was followed by the changes in viscosity of the substrate. Marked differences were observed. The characteristic of peptic caseinogen hydrolysis is the separation of an intermediate product containing P. The ratio P/N and hence probably the composition of this product for the various caseinogen preps. is approx. const. This phospho-

peptone is not identical with that obtained by tryptic digestion of caseinogen. Both the viscosity changes and the velocity of the titratable proteolytic fission depend on the P content of the original substrate.

J. H. BIRKINSHAW.

Determination of salivary urea. A. M. CENTENO (Presna med. Argentina, 1931, 17, 1751—1754).—Saliva is equal, or nearly equal, to blood-urea. In pathological conditions the increase in the saliva-urea is proportional to that of blood-urea.

CHEMICAL ABSTRACTS.

Urea-excreting function of the liver. I. M. SAKAI (Japan. J. Gastroenterol., 1931, 3, 316—328).—Liver-bile of rabbits contains 9, whilst bladder-bile contains 19, mg. of urea per 100 c.c. Intravenous injection of urea increases excretion by both liver and kidneys. Kidney injury is partly compensated by urea excretion by the liver. CHEMICAL ABSTRACTS.

Bile acid of wild pig's bile. S. SHIBUYA and T. MIKI (Z. physiol. Chem., 1932, 206, 279—281).—From the hydrolysed extract of the dried gall-bladder of the wild pig α -hyodeoxycholic acid and glycine were isolated, indicating the presence of glycohyodeoxycholic acid in the original material.

J. H. BIRKINSHAW.

Bile acid metabolism. V. Atophan chlororrhœa. I. SAKAMOTO and S. NAKAGAWA. VI. Bile acid secretion and blockage of the reticulo-endothelial system. H. MIKAMI and S. NAKAGAWA (J. Biochem. Japan, 1932, 15, 115—128, 129—149).—V. In dogs with fistulæ of the bile-duct or bladder the proportion of bilirubin and bile acid is fairly steady, whilst that of NaCl remains const. Following administration of atophan the amounts of bilirubin and bile acid secreted are unchanged despite the increased flow of bile. The action of atophan is not dependent on the autonomic nervous system, but is probably due to direct stimulation of the liver cells.

VI. Blockage of the reticulo-endothelial system by colloids produces a marked fall in the secretion of bile, whilst the change in bilirubin depends on the type of colloid used. The NaCl content is unchanged, the abs. amount being dependent on the amount of bile secreted.

F. O. HOWITT.

Bile acids and carbohydrate metabolism. XII. Influence of bile acids and the autonomic nervous system on liver-glycogenesis. T. MIKI. XIII. Influence of bile acids and internal secretions on liver-glycogenesis. K. FUGIWARA (J. Biochem. Japan, 1932, 15, 167—179, 181—192).—XII. The synergising action of Na cholate on liver-glycogenesis in starved rabbits is inhibited by section of the splanchnics or of the vagi, the inhibition being subsequently removed by administration of ergotamine. Thus the stimulating action of bile acids on liver-glycogenesis is related to the autonomic nervous system.

XIII. Na cholate antagonises the glycogenolytic action of adrenaline or phloridzin and synergises the glycogenetic influence of insulin. F. O. HOWITT.

Bile acid formation. V. Influence of feeding on the bile acid content of bile. T. FUKASE and K. FUGIWARA (J. Biochem. Japan, 1932, 15, 193—196).—In rabbits fed with "okara" (soya-bean oil?)

the bile is richer in glycocholic acid than in those fed on clover.

F. O. HOWITT.

Bilirubin and the van den Bergh reaction. F. S. FOWWEATHER (Biochem. J., 1932, 26, 165—182).—Cryst. bilirubin from gallstones, and its Na and NH₄ salts, give delayed van den Bergh reactions in serum. The pigment pptd. from the mother-liquor gives a direct reaction, as also do pigments obtained from fresh bile with and without acidification. These are regarded as free acid and salt. Directly reacting salts of bilirubin are pptd. from dil. alkaline solutions of cryst. bilirubin by alkaline salts. Bilirubin is regarded as existing in two forms, giving rise to two series of salts.

A. COHEN.

Poison of the skin-glands of the marble salamander (*Molge marmorata*). O. GESSNER (Arch. exp. Path. Pharm., 1932, 165, 350—374).—The secretion consists of a volatile, strongly irritating substance and two non-volatile constituents, one of which possesses agglutinating activity, the other being the main toxic element and having the following properties. It induces local irritation on superficial application, whilst parenteral administration causes intense hæmolysis, contraction of striped and smooth muscle, and finally death, the min. lethal dose for mice being 0.0054 mg. per g. The physical properties of this substance indicate a "sapotoxin."

F. O. HOWITT.

Mucoprotein as a normal constituent of gastric juice. D. R. WEBSTER and S. A. KOMAROV (J. Biol. Chem., 1932, 96, 133—142).—Gastric juice from dogs with gastric fistulæ contains a mucoprotein which has a higher N content and a lower reducing val. after hydrolysis than mucoproteins such as mucin from the submaxillary gland. Its non-identity with the mucin from the mucus of the gastric surface epithelium indicates a secretory product of the gastric glands. The relation of the mucin to pepsin is discussed.

F. O. HOWITT.

Gastric acidity in normal individuals. J. LERMAN, F. D. PIERCE, and A. J. BROGAN (J. Clin. Invest., 1932, 11, 155—165).—The average free acidity (after stimulation with histamine and EtOH) was 40.4 c.c. of 0.1N-acid, and the average total acidity 50.1, with no correlation between acidity and age. Anacidity was correlated with basal metabolism.

CHEMICAL ABSTRACTS.

Does wool-fat contain "hydroxycholestenol"? I. LIFSCHÜTZ (Arch. Pharm., 1932, 270, 205—207).—Substances described as "hydroxycholestenol" and the "saturated cyclic alcohol" (Frick, G.P. 458,198) are isocholesterol and the (aliphatic) derivative of lanoceric acid (A., 1896, i, 522), respectively.

R. S. CAHN.

Urinary protein excretion as a physico-chemical problem. F. MAINZER (Naturwiss., 1932, 20, 264—268).—The selective permeability of the human kidney to serum-albumin and globulin, hæmoglobin, and Bence-Jones protein is discussed with reference to their physico-chemical properties and also to those which possibly function in the living membrane.

F. O. HOWITT.

Bromide retention. K. O. MÖLLER (Arch. exp. Path. Pharm., 1932, 165, 244—260).—The urinary

Cl:Br ratio in rabbits is identical with the corresponding serum val. Depression of the Cl' storage produces a marked retention of injected Br' in order to normalise the osmotic pressure and halogen level of the serum. Up to 75% of the serum-Cl' in the rabbit can be replaced by Br' without causing death. Administration of theophylline to Br'-treated animals results in an increased excretion of Br' and, to an equal degree, of Cl', whereas with I'-treated animals no increased excretion of I' occurs. F. O. HOWITT.

Determination of dialkylbarbituric acids in urine. M. KLINGENFUSS and M. REINERT (Arch. exp. Path. Pharm., 1932, 165, 416—419).—The urine is pptd. by basic Pb acetate, excess of Pb removed by CO₂, and the Et₂O extract extracted with 0.1N-NaOH, the aq. extract being saturated with CO₂ and re-extracted with Et₂O. The second Et₂O extract is boiled with C, and the filtrate evaporated in presence of C₆H₆, yielding a cryst. residue which is weighed and identified by its m. p. Amounts of 10—100 mg. per litre are accurately determined by this method. F. O. HOWITT.

Determination of urea in urine by means of hydrolysis. S. L. LEIBOFF and B. S. KAHN (J. Lab. Clin. Med., 1931, 17, 77—78).—The urine is treated with permuted to remove NH₃, acidified, and digested under pressure for 10 min.; the N content is then determined by direct nesslerisation.

CHEMICAL ABSTRACTS.

Determination of [urinary] acetone by a steam-distillation method. L. DE SAINT-RAT and T. MENA (Bull. Soc. Chim. biol., 1932, 14, 317—326).—The apparatus and technique of the method are described. The method consists in treating the urine with basic Pb acetate and aq. NH₃, filtering, and passing steam through 5 c.c. of the filtrate for several min. The COMe₂ is collected in H₂O and determined iodometrically. β-Hydroxybutyric acid is determined by double treatment with K₂Cr₂O₇ of the solution left after the COMe₂ is removed, the COMe₂ formed being determined as before. A. LAWSON.

Determination of 8-hydroxyquinoline in urine in presence of phenol. F. LUTHER (Deut. med. Woch., 1931, 57, 1739; Chem. Zentr., 1932, i, 108).—Fission of 8-hydroxyquinoline takes place and part is eliminated as PhOH. An analytical method is described. A. A. ELDRIDGE.

Determination of glycuronic acid in urine and blood. M. HAENDEL (Rev. asoc. med. Argentina, 1929; 42, 215—220).—The glycuronic acid is pptd. from urine or deproteinised (Seegen) blood with ammoniacal Pb(OAc)₂; the ppt. is treated with HCl and the furfuraldehyde distilled in steam. KHSO₃ is added to the distillate and the excess determined iodometrically. CHEMICAL ABSTRACTS.

Bromine reaction of pregnancy urine. A. R. ARMSTRONG and E. WALKER (Biochem. J., 1932, 26, 143—146).—The isolation of the substance in the urine of pregnancy giving Knoop's Br-water test is described. It is identified as histidine. The test is regarded as sp. for histidine and N-methylhistidine. A. COHEN.

Detection of diastase in urine. J. WOHLGEMUTH (Biochem. Z., 1932, 247, 465).—The objection raised by Herzfeld (this vol., 79) can be overcome by the use of excess of I. There is no need to prepare an osazone, but the buffer solution must be prepared exactly as originally (A., 1930, 1207) described.

W. MCCARTNEY.

Effect of intensive function of sweat glands on the excretion of uric acid and phosphate in the urine. J. MELKA (Pflüger's Archiv, 1931, 228, 666—670; Chem. Zentr., 1932, i, 544).—Activity of the sweat glands is accompanied by increase in urinary uric acid and PO₄^{'''}. A. A. ELDRIDGE.

Spectrophotometric determination of urobilin and urobilinogen. L. HEILMEYER (Z. ges. exp. Med., 1931, 76, 220—235; Chem. Zentr., 1932, i, 108).—Urobilin is not a chemical individual. Its determination is possible only by way of urobilinogen by Terwen's method. The quant. absorption spectrum of the urobilinogen-MeCHO condensation product is const. A method for the determination of urobilinogen and the sum urobilin + urobilinogen is described. A. A. ELDRIDGE.

Excretory function of the liver. I. Uric acid. T. MATSUDA (Japan. J. Gastroenterol., 1931, 3, 293—307).—Of rabbits, the blood contains 1.2—1.5, urine 9—13, and bile 0.7—1.1 mg. of uric acid per 100 c.c. After intravenous injection of uric acid the rises in blood and bile are parallel. Kidney failure is incompletely compensated by increased elimination of uric acid by the liver.

CHEMICAL ABSTRACTS.

Physiology of excretion in a blood-sucking insect, *Rhodnius prolixus* (Hemiptera, Reduviidæ). I. Composition of the urine. III. Mechanism of uric acid excretion. V. B. WIGGLESWORTH (J. Exp. Biol., 1931, 8, 411—427, 443—451).—I. The urine is alkaline and contains large quantities of NaCl and KCl, with traces of urea, HCO₃['], SO₄^{''}, and uric acid; after the first day it becomes semi-solid and contains urates, Ca, Mg, SO₄^{''}, PO₄^{'''}, and creatine. All of the N is excreted as uric acid. CHEMICAL ABSTRACTS.

Phospholipins in the blood of infants and children. I. N. KUGELMASS and E. GREENWALD (Amer. J. Dis. Children, 1931, 42, 1134—1136).—The average val. (2.5 mg. per 100 c.c.) tends to remain const. irrespective of changes in tissue-phospholipin in disease. The val. may decrease in marasmus. CHEMICAL ABSTRACTS.

Alkalosis in the vomiting of infancy. M. MAIZELS (Arch. Dis. Childhood, 1931, 6, 293—302).—The obstructive vomiting of infancy is unaccompanied by alkalosis or marked reduction in blood-Cl'. An increase in plasma-HCO₃['] and a decrease in plasma- and cell-Cl' may accompany pyloric obstruction. CHEMICAL ABSTRACTS.

Glutathione content of anti-anæmic substances used in the treatment of pernicious anæmia. R. FLEMING (Biochem. J., 1932, 26, 461—463).—Commercial anti-anæmic products contain glutathione mostly in the oxidised form, whilst in fresh tissue (gastric mucosa of the pig) it is present more in the reduced form. S. S. ZILVA.

Certain metals in the prevention of nutritional anæmia in the rat. J. M. ORTEN, F. A. UNDERHILL, and R. C. LEWIS (*J. Biol. Chem.*, 1932, 96, 1—9).—Cu, but not Mn, Co, Ni, or Zn, either alone or admixed, has the power of preventing nutritional anæmia in rats fed a milk diet supplemented by inorg. Fe. F. O. HOWITT.

Action of cinchophen on the liver tract. E. P. C. WHITE (*J. Lab. Clin. Med.*, 1931, 17, 17—21).—Normal vals. were obtained for blood-non-protein-N, -uric acid, and -creatinine, icterus index, van den Bergh reaction, glucose and fructose tolerance test during continuous administration of cinchophen to arthritic patients who had no liver or pancreatic dysfunction. CHEMICAL ABSTRACTS.

Cholesterol content of lipins of carcinomas. R. WILHELM and G. FUCHS (*Biochem. Z.*, 1932, 247, 297—305).—Lipin from carcinoma cells (chiefly from liver) contains more cholesterol than does that from cells of normal parenchymatous organs. The difference is due to the sp. chemical composition of the cells. The connective tissue of tumours likewise has a high cholesterol content. W. McCARTNEY.

Hyperplastic reaction of the skin to thiol and its significance in neoplasia. S. P. REIMANN (*Amer. J. Cancer*, 1931, 15, 2149—2168).—The SH-SO₂ equilibrium forces cells to divide beyond their normal division levels. Malignancy is discussed in relation to stimulus by -SH and the chemical groups of chromosomes. CHEMICAL ABSTRACTS.

Analysis of tumour resistance. I. Enzymes. N. WATERMAN (*Z. Krebsforsch.*, 1931, 34, 313—326; *Chem. Zentr.*, 1932, i, 251).—Inactive pancreatic lipase is activated by serum at 60°. The activity of the substance in the serum is diminished by reduction with HSO₃'⁻, but increased by oxidation with H₂O₂. A. A. ELDRIDGE.

Modifying the respiration of tumours. I. By amino-acids. B. KISCH (*Biochem. Z.*, 1932, 247, 354—364; cf. this vol., 420, 643).—The respiration of fresh and old tissue from Jensen rat sarcoma and Ehrlich mouse carcinoma is sometimes increased by serine and by α-aminobutyric acid, whilst valine also occasionally increases slightly the respiration of the sarcoma tissue. Other NH₂-acids (and sarcosine) which increase respiration in healthy tissue (kidney, retina) have no effect on that of the diseased tissue. W. McCARTNEY.

Proteins of the lens in cataract. T. TSUJI (*J. Biochem. Japan*, 1932, 15, 33—64).—The proteins of the lens of the ox increase with increasing age. Experimental cataract in rabbits is accompanied by a decrease in total proteins and in β-crystallin (A., 1893, ii, 424) and by an increase in the "albumoid" and α-crystallin. In such animals and also in human cases the cysteine content is decreased and cystine, which normally is absent, appears. Other changes in the physico-chemical character of the lens-proteins are described. F. O. HOWITT.

Iodine content of food and incidence of goitre. L. SCHEFFER (*Biochem. Z.*, 1932, 247, 418—423).—Although goitre is prevalent (10% of the population suffer) in Pécs (Hungary) the food and H₂O consumed

by the inhabitants contain more I than is required to prevent the onset of the disease. Hence doubt is cast on the validity of the theory that goitre is caused by lack of I. W. McCARTNEY.

Biological value, iodine content, histological, structural, and clinical picture of goitre. A. JORDI (*Arch. Int. Med.*, 1932, 49, 541—577).—26 cases of goitre in California are described. Adenomas with hyperfunction differ biologically from diffuse goitre of primary Basedow's disease, the relation between biological activity and I content being const. only in the former. A. LAWSON.

Gastric secretion in exophthalmic goitre and myxœdema. J. LERMAN and J. H. MEANS (*J. Clin. Invest.*, 1932, 11, 167—182).—The frequency of anacidity is out of proportion to the lowered average acidities, suggesting a threshold of gastric secretion. In exophthalmic goitre there is correlation between the incidence of achlorhydria, but not between gastric acidity and other factors. CHEMICAL ABSTRACTS.

Congestive heart failure. XIII. Relation of dyspnoea of exertion to oxygen saturation and acid-base condition of the blood. G. E. CULLEN, T. R. HARRISON, J. A. CALHOUN, W. E. WILKINS, and M. M. TIMS. XIV. Orthopnoea; relation to ventilation, vital capacity, oxygen saturation, and acid-base condition of arterial and jugular blood. J. A. CALHOUN, G. E. CULLEN, T. R. HARRISON, W. L. WILKINS, and M. M. TIMS (*J. Clin. Invest.*, 1931, 10, 807—831, 833—855).—XIII. With mild exercise in congestive heart failure there are no significant changes in blood-p_H, CO₂ content and tension. Administration of NH₄Cl caused a large decrease in p_H and slight increase in ventilation. Max. exertion in normal subjects caused reduction in p_H and CO₂ content.

XIV. The increased respiratory rate is not due to changes in oxidation or acid-base balance.

CHEMICAL ABSTRACTS.

Physiology, correlations, and technique of the van den Bergh reaction, icterus index, and quantitative serum-bilirubin. N. W. ELTON (*J. Lab. Clin. Med.*, 1931, 17, 1—13).—A direct positive van den Bergh reaction is obtained when the suspensoid colloid and the unstable crystalloid form of bilirubin are both present in the blood-serum. Minute quantities of the crystalloid form suffice. The lengths of the delay periods indicate intermediate stages in the transition nascent → crystalloid bilirubin. The icterus index is not directly proportional to the serum-bilirubin. At an icterus index of 16.6, colloidal bilirubin may accumulate in the bloodstream; this causes no increase in colour intensity until the physical change indicated by development of the immediate type of van den Bergh reaction occurs. Methods for carrying out the three determinations in continuity with a small quantity of serum are described. CHEMICAL ABSTRACTS.

Ketosis. I. Sexual variation in starvation ketosis. H. J. DEUEL, jun., and M. GULICK (*J. Biol. Chem.*, 1932, 96, 25—34).—During fasting a greater degree of ketosis is developed in the female than in the male, as indicated by the excretion of ketones in the

urine and by the fall in CO_2 -combining power of the blood. The decrease and subsequent increase in N excretion are due to the sparing action of the residual tissue-glycogen and, whilst occurring in both sexes, are more prolonged in the male. F. O. HOWITT.

Chemistry of the blood of dairy cows before and after parturition and its relation to milk-fever. L. T. WILSON and E. B. HART (J. Dairy Sci., 1932, 15, 116—131).—The Ca and P of cows' blood falls slightly within the first 3 days of calving, the effect being more definite in the case of second and later calves. The essential factor in milk-fever is a deficiency of blood-Ca. Plasma-phosphatase varies considerably about the time of calving. Phosphatase activity in milk is normally higher than that of plasma and in heavily milking cows is greater at the end than at the beginning of lactation. A. G. POLLARD.

Potassium and chronaxie in experimental muscular degeneration. A. LEULIER, B. POMME, and A. RICHARD (Compt. rend., 1932, 194, 1280—1282).—The degeneration in the muscles of rabbits which follows section of the sciatic is accompanied by an increase in chronaxie and a simultaneous but proportionately smaller decrease in K content. W. O. KERMAK.

Plasma-proteins in relation to blood hydration. VI. Serum-proteins in nephritic oedema. VII. Proteins in acute nephritis. J. P. PETERS, F. S. BRUCKMAN, A. J. EISENMAN, P. N. HALD, and A. M. WAKEMAN. VIII. Serum-proteins in heart disease. S. A. PAYNE and J. P. PETERS. IX. Serum-proteins in the terminal stages of renal disease. J. P. PETERS, F. S. BRUCKMAN, A. J. EISENMAN, P. N. HALD, and A. M. WAKEMAN (J. Clin. Invest., 1931, 10, 941—973; 1932, 11, 97—102, 103—112, 113—122).—VI. Reduction of serum-protein at the expense of the albumin fraction is common in nephritis with non-cardiac oedema, but not in idiopathic nephrosis. The chief causes of serum-protein deficiency are albuminuria and depletion of protein stores in the body.

VII. Lowering of serum-albumin is referable to leakage of albumin into the urine or to malnutrition. High serum-globulin is frequently found.

VIII. Oedema is generally associated with albumin deficiency referable to malnutrition.

IX. Reduction of serum-proteins, particularly the albumin fraction, is common, without correlation between albumin deficiency and oedema. CHEMICAL ABSTRACTS.

Comparison of the racemisation curves for urinary, oedema fluid, and blood-plasma proteins. J. W. CAVETT and R. B. GIBSON (J. Clin. Invest., 1931, 10, 857—867).—The rate of racemisation of albumins and pseudoglobulins of nephritic urines is the same as that of the corresponding serum-proteins. Blood-pseudoglobulin of a nephritic patient gave a rate identical with that of normal blood. CHEMICAL ABSTRACTS.

Nutritional oedema. Relation of the serum-proteins to the occurrence of oedema and to the effect of certain inorganic salts. A. A. WEECH and S. W. LING (J. Clin. Invest., 1931, 10, 869—888).—Oedema appeared at serum-albumin levels below

2.5, but not above 2.9, g. per 100 c.c.; there was no relation between globulin and oedema. Administration of NaCl and NaHCO_3 depressed Cl' excretion; Na is more nearly related than Cl' to the cause of oedema. CHEMICAL ABSTRACTS.

Variations in serum-calcium, -protein, and -inorganic phosphorus in early and late pregnancy, during parturition and the puerperium, and in non-pregnant women. W. F. OBERST and E. D. PLASS (J. Clin. Invest., 1932, 11, 123—127).—Correlation between serum-Ca and -protein in pregnant and puerperal women disappears in late pregnancy and parturition. No correlation between serum-Ca and -P was observed. CHEMICAL ABSTRACTS.

Mineral exchanges in man. III. Mineral metabolism during treatment of polycythaemia vera. S. H. BASSETT, T. KILLIP, and W. S. MCCANN (J. Clin. Invest., 1931, 10, 771—785).—Administration of acetylphenylhydrazine reduced the blood vol., cell vol., haemoglobin, and red cells. The large increase in endogenous Fe metabolism did not result in loss of body-Fe. During increased Fe excretion (probably haemoglobinuria) there is a decrease in faecal Fe which more than compensates for that found in the urine. Marked loss of N accompanies blood destruction. No significant changes in P, Mg, and Ca could be demonstrated. CHEMICAL ABSTRACTS.

Experimental hypotrophic rickets. G. MOURIQUAND, A. LEULIER, and L. WEILL (Compt. rend., 1932, 194, 1201—1202).—Hypotrophic rickets may be produced experimentally in animals placed on Pappenheimer diet, no. 85, if a "defixing" agent such as Sr or Mg is administered. This results in a loss of Ca from the animals and a retardation of growth or actual loss of wt. Rickets may thus be produced in the absence of rapid growth. W. O. KERMAK.

Calcium and phosphorus metabolism in late rickets. G. C. LINDER and D. G. M. VADAS (Lancet, 1931, 221, 1124—1126).—In a case of late rickets with a partial hyperparathyroid syndrome excision of the parathyroid relieved pain without affecting the Ca-P metabolism. L. S. THEOBALD.

Phosphorus and rickets. I. Sources of inorganic phosphorus in the treatment of experimental rickets. R. LECOQ and F. VILLUIS (J. Pharm. Chim., 1932, [viii], 15, 393—397).—With rats, the antirachitic activity of CaHPO_4 , Na_2HPO_4 , $\text{Ca}_2(\text{HPO}_4)_2$, $\text{Ca}_3(\text{PO}_4)_2$, NaH_2PO_4 , and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ falls in this order, the last two salts being inactive even in the highest concn. studied (3% of diet). $\text{Zn}_3(\text{PO}_4)_2$, in so far as it can be tolerated by the animals, is inactive. A. LAWSON.

Calcium and phosphorus studies. I. Effect of calcium and phosphorus of the diet on tetany, serum-calcium, and food intake of parathyroidectomised rats. II. Effect of diet and of viosterol on the tetany and on the serum-calcium of parathyroidectomised rats. III. The source of excess serum-calcium in viosterol hypercalcaemia. D. H. SHELLING (J. Biol. Chem., 1932, 96, 195—214, 215—228, 229—243).—I. In parathyroidectomised rats low-Ca and high-P diets produce

tetany, whilst high-Ca and low-P diets relieve it and the accompanying anorexia. Serum-Ca depends on Ca and P intake and on severity of tetany. Excess P, administered as Na_2HPO_4 or $\text{Na}_2\text{P}_2\text{O}_7$, causes anorexia, but is ineffective as NaPO_3 or NaH_2PO_2 .

II. With low-Ca diets, parathyroid tetany is relieved by fairly large doses of viosterol, and such doses can raise serum-Ca from tetanic to hypercalcaemic levels even when no Ca or P is ingested. The activity of viosterol may therefore be independent of the parathyroid. Injection of parathormone into rachitic rats causes further bone decalcification.

III. Viosterol hypercalcaemia may be induced in rats fed on Ca-free diets, and more readily if P is also absent. It is accompanied by excess Ca excretion by the kidney in the latter case and as phosphate in the faeces if excess P is fed. The animals show histological and X-ray evidence of bone decalcification.

J. B. BATEMAN.

Calcium and phosphorus metabolism. VI. In hypoparathyroidism and chronic steatorrhoea with tetany. J. C. AUB, F. ALBRIGHT, W. BAUER, and E. ROSSMEISL. XV. In various metabolic diseases. J. C. AUB and R. F. FARQUHARSON (J. Clin. Invest., 1932, 11, 211—234, 235—248).—VI. In tetany associated with chronic steatorrhoea there is low serum-P and high partition of P in the urine as compared with the faeces; disordered Ca and P metabolism is due to decreased Ca absorption. Thyroid medication in hypoparathyroidism causes a rise in serum-Ca and increased urinary excretion of Ca and P. In hypoparathyroidism the Ca on being removed from the bones by the thyroid hormone is below the level necessary for excretion.

XV. Ca and P may be liberated in one part and deposited in another part of a bone. In chronic bone diseases and jaundice the variations from normal in Ca and P excretion were slight.

CHEMICAL ABSTRACTS.

Accumulation of iron in tuberculous areas. II. V. MENKIN (J. Exp. Med., 1932, 55, 101—108).—Repeated intravenous injection of FeCl_3 increases the survival time of tuberculous rabbits.

CHEMICAL ABSTRACTS.

Metabolism of the Chinese. I. Body surface. H. NECHELES and C. T. LOO. II. Basal metabolism. H. NECHELES. III. Specific dynamic action. H. NECHELES and C. T. LOO. IV. Basal metabolism and methods. H. NECHELES (Chinese J. Physiol., 1932, 6, 129—152, 153—174, 175—200, 201—224).

Technique for studying metabolism of rats. V. KORENCHESKY and M. DENISON (Biochem. J., 1932, 26, 147—150).

Food requirements of pregnancy in swine. H. H. MITCHELL, W. E. CARROLL, T. S. HAMILTON, and G. E. HUNT (Illinois Agric. Exp. Sta. Bull., 1931, No. 375, 467—504).—The rate of deposition of nutrients in the contents of the uterus with the advancing time of gestation is expressed mathematically. In the gilts examined no tendency was indicated for the retention of nutrients in the body increase as the period of gestation advanced. A. G. POLLARD.

Effect of amino-acids on respiration of tissues. V. β -Aminopropionic acid and α -aminobutyric acid. B. KISCH (Biochem. Z., 1932, 247, 365—370; cf. this vol., 420).—The respiration of tissue from the kidney, liver, and retina of the rat, guinea-pig, rabbit, cat, and ox is increased by β -aminopropionic and α -aminobutyric acid. The former acid is less active than is alanine, especially in the case of old tissue from rat kidney. In general, butyric acid is less active than is its α - NH_2 -derivative. W. McCARTNEY.

Change of reaction of muscle in relation to development of tension and chemical change. O. MEYERHOF, W. MÖHLE, and W. SCHULZ (Biochem. Z., 1932, 246, 285—318).—At a given pressure of CO_2 muscle tissue is not isohydric with a Ringer's solution containing an equiv. amount of HCO_3^- . The deviation from Hasselbalch's equation is due to a change of p_K (CO_2) caused by the presence of buffers. The large CO_2 -uptake of iodoacetic acid-poisoned muscle in rigor from HCO_3^- -Ringer's solution is due to the diffusion of the buffer-substances into the surrounding fluid. H. W. DUDLEY.

Yeast and casein supplements to corn and soya-bean rations for rats and swine. C. L. SHREWSBURY, C. M. VESTAL, and S. M. HAUGE (J. Agric. Res., 1932, 44, 267—274).—Casein supplements a maize but not a soya-bean ration, whilst dried yeast does not supplement either to an economic extent. Cooked beans are of greater nutritive val. than raw beans. P. G. MARSHALL.

Feeding experiments with decomposition products of proteins. S. MAYEDA (Proc. Imp. Acad. Tokyo, 1932, 8, 98—101).—Normal growth was obtained for 6 months in rats fed on a diet containing 8% of H_2SO_4 -hydrolytic product of fish protein and 8% of $\text{Ba}(\text{OH})_2$ -hydrolytic product, but devoid of protein. Oryzanin or EtOH extract of yeast was used as the source of vitamin-B. Growth was also maintained for 50 days with acid decomp. products alone, provided that 3% of *r*-tryptophan was added. P. G. MARSHALL.

Optimum protein content of rations for growing chicks. R. W. SWIFT, A. BLACK, L. VORIS, and E. M. FUNK (Poultry Sci., 1931, 10, 288—298).—The digestibility of protein was not markedly influenced by the level of protein intake. When the ration contained 14.74—15.31% of protein the protein, but not the whole ration, was most efficiently utilised. With 14.74—24.83% of protein the feed was most efficiently utilised to produce gain in wt., whereas greatest total gain in wt. was produced by rations containing 20—22% of protein. Data on N-retention, digestibility, and composition of feed are tabulated. P. G. MARSHALL.

CHEMICAL ABSTRACTS.

Metabolism of phospholipins. V. Relationship between the amount of fat ingested and the degree of unsaturation of the phospholipins and neutral fat in the tissues of the rat. R. G. SINCLAIR (J. Biol. Chem., 1932, 96, 103—125).—The addition of cod-liver oil to the diet of rats on a fat-free diet results in a marked and proportional increase in the I val. of the phospholipin fatty acids, especially of those of the liver, but in only a slight increase in that of the neutral fatty acids. This phenomenon also

occurs with lard and, to a smaller extent, with coconut oil. The bearing of this unsaturation on growth and fat metabolism is discussed. F. O. HOWITT.

Autolysis and production of acetaldehyde in adrenalectomised cats. A. SIMON and B. KOLONITS (Biochem. Z., 1932, 247, 476—481).—In the livers of the cats autolysis is more extensive and in their muscles the production of MeCHO from glycogen is less pronounced than with normal cats.

W. MCCARTNEY.

Micro-electric investigation of intestinal re-sorption. Transport of sugar in the portal vein and in the lymph. R. KELLER (Biochem. Z., 1932, 247, 466—473).—The importance of the liver-glycogen as a source of energy has been over-estimated, since the lymph is also concerned, sometimes to a greater extent than is the portal vein, in the transport of sugar from the intestine.

W. MCCARTNEY.

Nutritional value of bread. III. Assimilation of the carbohydrate of various kinds of bread in the animal body. I. ABELIN and A. BIDERBOST (Biochem. Z., 1932, 247, 429—444; cf. A., 1931, 648).—As regards the resorption by rats of the carbohydrate which they contain white and wholemeal breads do not differ. In those breads about 99% and in other kinds of bread (rye etc.) 93—97% of the carbohydrate is resorbed. No matter which kind of bread is consumed, the resulting storage of glycogen in the rats is about the same, but differences are observed in the resulting changes in the amounts of glycogen in the liver. The causes of these differences are unknown. W. MCCARTNEY.

Metabolism of normal and tumour tissue. V. Carbon dioxide retention of serum: its use in the measurement of tissue glycolysis. F. DICKENS and F. ŠMER (Biochem. J., 1932, 26, 90—98).—The CO₂ retention of normal and dialysed serum and of Warburg's "serum-model" is approx. linearly related to p_H change between p_H 7.0 and 7.7. This result is applicable to the measurement of production or consumption of org. acids by tissues in serum.

A. COHEN.

Carbohydrate metabolism in birds. Site of the biochemical lesion in avian polyneuritis. N. GAVRILESCU, A. P. MEIKLEJOHN, R. PASSMORE, and R. A. PETERS (Proc. Roy. Soc., 1932, B, 110, 431—447).—Various parts of the brain of normal pigeons and of pigeons suffering from advanced B₁-avitaminosis were examined for O₂-uptake in Ringer-PO₄ solution alone and in presence of glucose, lactate, or succinate. No significant differences between normal and avitaminosis brain-tissue occur in the residual oxidation, the val. of which varies somewhat, due to varying amounts of unknown substances present as substrate in addition to the greater proportion of preformed lactic acid. The O₂-uptake for both normal and avitaminosis brain attains a max. with approx. 0.037*M*-lactate, whilst with succinate the max. is at approx. 0.18*M*. Its val. in 0.037*M*-lactate is decreased in avitaminosis both for cerebral and optic lobe tissue, a return to normal occurring on addition of vitamin-B₁ concentrates. Similar phenomena occur with glucose

but not with succinate. Addition of B₁ concentrates to normal tissue in presence of lactate results in only a slight increase of O₂-uptake. Hence in the pathological condition of avian polyneuritis there occurs a lesion not affecting all oxidase systems, but associated with lactate. The vitamin cannot be considered as part of the respiratory enzyme or cytochrome system, although it forms an integral part of an oxidase system and constitutes a true factor in the intermediary metabolism of carbohydrate.

F. O. HOWITT.

Bile acids and carbohydrate metabolism. XIV. Production of glycogen in the liver by bile acids given together with adrenaline or insulin. Influence of the vegetative nervous system. XV. Production of glycogen in muscle by bile acids following section of the splanchnic nerves. T. MIKI (Biochem. Z., 1932, 247, 445—458, 459—464; cf. this vol., 639).—XIV. In rabbits administration of adrenaline increases and that of insulin decreases the production of glycogen in the liver if the splanchnic nerves are cut. Cholic acid, administered at the same time, causes increase in both cases, but the increase with adrenaline is much greater than is that with insulin and exceeds that due to cholic acid alone. The results of section of the vagus nerves are similar but much less pronounced. It follows that, in the liver, mobilisation of glycogen is dependent on increased sympathetic tonus and synthesis of glycogen on decreased sympathetic tonus. Possibly the effect produced by insulin is due to increased peripheral oxidation of sugar resulting from over-stimulation of the vagus nerves which increases the secretion of insulin in the pancreas. The stimulating action of cholic acid and of adrenaline depends more on the tonus of the sympathetic than on that of the vagus nerves, whilst the opposite is true for the action of insulin. Moreover, there is synergy between the actions of cholic acid and adrenaline, but antagonism between those of the acid and insulin.

XV. Production of glycogen in the muscles of rabbits is increased by administration of small amounts of adrenaline or of cholic acid if the splanchnic nerves are cut. Simultaneous administration of the two substances with section of these nerves results in a production of glycogen in the muscles which is greater than that due to adrenaline alone but less than that due to cholic acid alone.

W. MCCARTNEY.

Ligation of the parotid duct and carbohydrate metabolism. L. M. ZIMMERMAN and S. SOSKIN (Arch. Int. Med., 1932, 49, 663—665).—Ligation of the parotid ducts of totally depancreatised dogs has no effect on the carbohydrate metabolism as indicated by the N and glucose content of the urine.

A. LAWSON.

Carbohydrate changes during anaërobiosis of mammalian muscle. G. T. CORI (J. Biol. Chem., 1932, 96, 259—269).—Analyses on extirpated gastrocnemii of rats before and after anaërobiosis in N₂ at 37° showed that glycogen breakdown is nearly balanced by formation of lactic acid and hexose-phosphate. There was no accumulation of hexose-diphosphate during anaërobiosis. J. B. BATEMAN.

Glycogenesis. F. RATHERY, S. GIBERT, and Y. LAURENT (Bull. Soc. Chim. biol., 1932, 14, 327—368).—In dogs fed on normal diets, in starved animals, and in those in which hepatic glycogen has almost completely disappeared, the administration of large amounts of glucose causes in most cases an increase in hepatic glycogen, but sometimes a decrease. The glucose content of the portal vein shows the liver to be receiving glucose, but a comparison of the glucose content of the portal vein with the amounts of hepatic and muscle-glycogen shows that complete transformation of the glucose into glycogen does not take place. There are probably sources of stored carbohydrate in the liver other than glycogen.

A. LAWSON.

Physiological behaviour of the trioses and of related compounds. I. Increase of liver-glycogen after feeding methylglyoxal and pyruvic acid. II. Increase of liver-glycogen after feeding glyceraldehyde. R. STÖHR (Z. physiol. Chem., 1932, 206, 15—24, 211—216).—I. COMe·CHO fed to fasting rats in doses of 100 mg. per 100 g. body-wt. produces an increase in liver-glycogen; with 150—200 mg. glycogen is strongly diminished, probably owing to lactic acid formation. In general COMe·CHO was absent from the blood 3 hr. after the dose; the blood-sugar did not vary to any extent.

II. The feeding of 0.2—0.3 g. of glyceraldehyde per 100 g. of body-wt. to fasting rats produced an increase in liver-glycogen (from 0.051 to 0.792 g. per 100 g. of liver). The blood-sugar was either unchanged or showed a large increase; glyceraldehyde had disappeared from the blood in 3 hr. The phosphoric-molybdic acid reagent of Folin gives a blue colour with glyceraldehyde, which can then be determined by titration with KMnO_4 to disappearance of the colour.

J. H. BIRKINSHAW.

Action of methylglyoxal on acetoacetic acid. III. The ketol ($\text{C}_6\text{H}_{10}\text{O}_3$) as glycogen-former. R. STÖHR and M. HENZE (Z. physiol. Chem., 1932, 206, 1—14; cf. A., 1931, 69).—After administration of the ketol $\text{C}_6\text{H}_{10}\text{O}_3$ to fasting rats the liver-glycogen increased considerably; the glycogen storage was independent of the quantity resorbed. Higher doses of the ketol, by their toxic action, lowered the glycogen content. The ketol is probably first oxidised to the triketone COMe·CO·CH₂·COMe, which breaks up into two 3-C units both capable of producing glycogen. The ketol produces a slight increase in the blood-sugar. A method was evolved for the determination of the ketol in blood in presence of blood-sugar.

J. H. BIRKINSHAW.

Behaviour of the carbohydrates and lactic acid of the muscle of haddock (*Gadus aeglefinus*) after death. N. L. MACPHERSON (Biochem. J., 1932, 26, 80—87).—Immediately after death the glycogen content of haddock muscle is 0.4—0.6%. This rapidly falls in a few hr. and then more slowly to <0.1 of the original val. in 24 hr. The sugar content is 0.05% if extracted with aq. EtOH, and 0.01% if determined by adsorption on CuSO_4 and CaO, or extracted with $\text{CCl}_3\text{CO}_2\text{H}$. Acid hydrolysis doubles the reducing power of EtOH extracts. The lactic acid content is 0.08%, which increases to 0.17% in

40 hr. The lag in lactic acid production during glycogen disappearance indicates an intermediate which is not a polysaccharide, since no increase in the original vals. of free sugar before and after hydrolysis is observed.

A. COHEN.

Lactic acid production in isolated rabbit's intestine. M. TAKAHASHI (Sei-ikwai Med. J., 1931, 50, No. 2, 24—85).—Drugs which stimulate intestinal movement produce more lactic acid than those which depress it; in both cases the amount was subnormal. Except with acetylcholine and adrenaline, the intestinal movement and lactic acid production are parallel. Except with acetylcholine the p_{H} of the liquid is proportional to the amount of lactic acid found. The lactic acid content of the small intestine varies with the locality; the average is 92.18 mg. per 100 g.

CHEMICAL ABSTRACTS.

Lactic acid metabolism. II. Lactic acid content of the blood of different animals. F. MATAKAS (Arch. exp. Path. Pharm., 1932, 165, 221—229).—Rabbits, pigeons, and fowls show a greater variation in the resting blood-lactic acid level than do cats, dogs, goats, or sheep. The variations are not due to the experimental conditions, but are characteristic of the animal. Hence these three animals are unsuitable for the study of lactic acid metabolism.

F. O. HOWITT.

Relationship between chemical structure and physiological response. I. Conjugation of substituted benzoic acids. A. J. QUICK and M. A. COOPER (J. Biol. Chem., 1932, 96, 83—101).—Various derivatives of BzOH, α -naphthoic acid, and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ were neutralised, fed to dogs, and the conjugation of the compounds excreted in the urine was determined. Substitution of BzOH in the *o*-position greatly inhibits its conjugation with glycine, the effect being independent of the nature of the group, whereas for conjugation with glycuronic acid an acidic group diminishes and a basic group increases the excretion, whilst a neutral group has little effect. An opposite but less marked effect occurs with *m*-substitution, whilst *p*-substitution more closely resembles the *o*-. The dissociation const. of the substituted BzOH is related to the rate at which it is excreted combined with glycuronic acid.

F. O. HOWITT.

Site of the synthesis of hippuric acid and phenylacetic acid in the dog. A. J. QUICK (J. Biol. Chem., 1932, 96, 73—81).—Hippuric acid is synthesised by the action of an enzyme ("hippuricase"), which in the dog is present only in the kidney but in the rabbit occurs in other organs. "Phenylaceticase," the enzyme which produces phenylacetic acid, occurs in the kidney and also in other organs of the dog. Injection of hippuric acid into nephrectomised dogs is followed by a gradual disappearance of the acid from the blood and replacement by BzOH and glycuronic acid monobenzoate. Hence there exists a separate enzyme ("histozyme") for the hydrolysis of hippuric acid.

F. O. HOWITT.

Behaviour of lactacidogen in muscular work. G. KRAFT (Z. physiol. Chem., 1932, 206, 155—167).—In confirmation of previous results (this vol., 188),

exhaustive stimulation of isolated frog's gastrocnemius in summer decreases, and in winter increases the lactacidogen. In the living frog, exhaustive stimulation always decreases the lactacidogen. After short stimulation of the living frog there is an increase in lactacidogen accompanied by lactic acid accumulation and fatigue. With continued stimulation the lactic acid again decreases and the fatigue passes off.

J. H. BIRKINSHAW.

Vital need of the body for certain unsaturated fatty acids. I. Experiments with fat-free diets in which sucrose furnishes the sole source of energy. H. M. EVANS and S. LEPKOVSKY (J. Biol. Chem., 1932, 96, 143—156; cf. A., 1929, 853).—Production of a sp. deficiency disease on rigidly fat-free diets is confirmed, characterised by impairment of growth, dermatitis, disturbed H₂O metabolism, and hæmaturia. The condition is cured by maize starch and rice starch, by the fatty acids extracted from them, and by linoleic acid. Vitamin-B-deficiency as cause is definitely excluded. Potato starch and glycogen are ineffective.

J. B. BATEMAN.

Physiological action of phytosteryl esters. J. NIKUNI (J. Agric. Chem. Soc. Japan, 1931, 7, 827—838).—The growth responses of mice fed with cholesteryl and phytosteryl acetate and palmitate were compared. When large quantities of sterols were fed, only small quantities were deposited in the body. Cholesteryl esters are stored to a greater extent than phytosteryl esters.

CHEMICAL ABSTRACTS.

Cystine metabolism. G. SCOZ (Atti R. Accad. Lincei, 1931, [vi], 14, 586—589).—Feeding experiments with rats and puppies show that cystine has a distinct positive influence on general body and on hair-growth.

T. H. POPE.

Metabolism of *i*-cystine in the rat. N. R. LAWRIE (Biochem. J., 1932, 26, 435—440).—The rat can oxidise *i*-cystine as rapidly and completely as *l*-cystine. The val. of *i*-cystine for tissue-building purposes in the rat is $\frac{1}{3}$ — $\frac{2}{3}$ of that of *l*-cystine.

S. S. ZILVA.

Is preformed cystine essential to sheep for wool production? C. RIMINGTON and J. G. BEKKER (Nature, 1932, 129, 687—688).—A discussion.

L. S. THEOBALD.

Sulphur metabolism. R. SATO (Sei-i-kwai Med. J., 1930, 49, No. 8, 1—51).—The average S distribution in the urine of normal rabbits was: total S 0.6002, neutral S 0.1881, total SO₄ 0.4117, inorg. SO₄ 0.3796, ethereal SO₄ 0.0338 g.; increases following experimental icterus are recorded. The average total S contents for normal rabbits were: liver 1.30, lung 1.33, heart 1.43, kidney 1.30, testicles 0.85, spleen 1.33, adrenals 0.88, muscles 1.16%. The effects of injection of glucose and insulin are recorded.

CHEMICAL ABSTRACTS.

Growth reaction of embryonic marine forms to thiol and sulphoxide. D. M. HAMMETT and F. S. HAMMETT (Protoplasma, 1932, 15, 59—70).—The embryonic development of 5 species of marine organisms is accelerated by the SH group and retarded by the S:O group.

A. G. POLLARD.

Calcium and phosphorus requirements of dairy cows. I. Weekly balances through lactation

and gestation periods. H. B. ELLENBERGER, J. A. NEWLANDER, and C. H. JONES (Vermont Agric. Exp. Sta. Bull., 1931, No. 331, 27 pp.).—Negative Ca and P balances appear to be normal during the early stages of lactation and are compensated by rapid storage as the lactation and gestation periods advance. Feeding of mineral supplements reduced the periods of negative balance.

A. G. POLLARD.

Calcium and phosphorus metabolism of infants receiving undiluted milk. M. VAN K. NELSON (Amer. J. Dis. Children, 1931, 42, 1090—1099).—More Ca and P is retained than by infants receiving diluted milk or undernourished.

CHEMICAL ABSTRACTS.

Calcium and phosphorus requirements for growing chicks. I. Salt mixtures under rachitic conditions. II. Natural minerals. W. C. TULLY, S. M. HAGUE, C. W. CARRICK, and R. E. ROBERTS (Poultry Sci., 1931, 10, 299—309, 310—318).—I. Variations of McCollum's mineral diet no. 185 with a wide Ca : P ratio variation produced satisfactory growth and bone formation only when vitamin-D was present.

II. Mixtures of steamed bone meal with oyster shell or limestone were superior to mixtures of CaCO₃ and Ca₃(PO₄)₂ as sources of Ca and P in the absence of vitamin-D.

CHEMICAL ABSTRACTS.

Avertin. H. J. STANDER (Amer. J. Obstet. Gynecol., 1931, 22, 219—224).—Avertin (100 mg. per kg.) produced no change in (women's) blood-nitrogen-N, -urea-N, -uric acid, -lactic acid, -creatinine, -Cl, or -CO₂ combining power, and only a slight increase in -sugar. In dogs, 500 mg. per kg. produced no significant blood changes.

CHEMICAL ABSTRACTS.

Partition of chloroform in the hen's egg during intoxication of the embryo by this anæsthetic. Order of magnitude of the toxic cellular dose. S. LALLEMAND (Compt. rend., 1932, 194, 1396—1397).—When hens' eggs are kept for several days in an atm. of CHCl₃ saturated at 18°, the concn. of CHCl₃ in the white and yolk is 6 mg. and 65 mg. per g., respectively. At the time of the death of the embryo the concn. of CHCl₃ in the latter is probably about 2.4—2.7 mg. per g., which corresponds with an amount of 3 × 10⁻⁹ mg. of CHCl₃ per cell.

W. O. KERMAK.

Influence of homatropine, hyoscyamine, and scopolamine on the sugar mobilisation in the toad's liver produced by adrenaline. M. NAKANO (Folia Pharmacol. Japon., 1931, 13, No. 1, 42—77).—The alkaloids act on the sugar stores in the liver and behave like atropine towards glycogenolysis and glycogen mobilisation caused by adrenaline.

CHEMICAL ABSTRACTS.

Influence of the Δ²-cyclopentyl radical in the hypnotics of the barbituric acid series. Pharmacodynamics of Δ²-cyclopentylallylbarbituric acid. R. CHAUX (Compt. rend., 1932, 194, 1193—1195).—A second substituent in the 5-position of 5-Δ²-cyclopentylbarbituric acid increases the hypnotic activity on rabbits of the resulting compounds in the order Ph < Bu^α < Pr^α < β-bromoallyl, Et < Δ²-cyclopentyl < allyl, all the compounds being more active than veronal (5:5-diethylbarbituric acid) except the first.

W. O. KERMAK.

Combustion of alcohol in homeotherms. M. NICLOUX (Compt. rend., 1932, 194, 1390—1391).—In white mice at 30° to which EtOH has been administered subcutaneously the rate at which the EtOH is combusted in each animal is const. and independent of the quantity administered, but proportional to the wt. of the animal. The average quantity of EtOH burnt per g. animal per hr. is 0.65 mg., which it is proposed to name the const. of Et oxidation.

W. O. KERMACK.

Influence of various drugs on sugar mobilisation in the liver. Y. KAGAWA (Japan. J. Med. Sci., 1931, 5, No. 3, 113—138).—Alcohols, chloral hydrate, and Na barbital (1—5%) increase the sugar production of toads' livers; quinine, HgCl₂, and H₃AsO₃ in low concn. cause no increase. PrOH (0.3%) inhibits sugar mobilisation by adrenaline; EtOH, Et₂O, quinine, HgCl₂, and H₃AsO₃ do so only at certain concns., and increase the effect at other concns.

CHEMICAL ABSTRACTS.

Effect of alcohol on the oxygen uptake of brain tissue. J. D. ROBERTSON and C. P. STEWART (Biochem. J., 1932, 26, 65—74).—Following EtOH administration to rabbits the O₂ uptake of brain tissue increases (more in grey matter than in white) for about 1 hr. and then falls slightly below normal.

A. COHEN.

Effect of irradiated amino-acids on the vascular action of adrenaline. S. FREYTAG (Pflüger's Archiv, 1931, 229, 226—235; Chem. Zentr., 1932, i, 830—831).—Irradiation of alanine increases its depressant action on the vascular action of adrenaline; with arginine the depressant substance is produced only when the irradiated solution is evaporated. Glutamic acid is unchanged.

A. A. ELDRIDGE.

Can the sympatholytic poisons transform, into a vaso-dilator action, the vaso-constrictor action of amines of which they do not reverse the pressor action? RAYMOND-HAMET (Compt. rend., 1932, 194, 1529—1532).—A sec.-amine such as *p*-OH·C₆H₄·CH(OH)·CH₂·NHMe which has normally a vaso-constrictor action produces vaso-dilatation in presence of yohimbine methosulphate, although ergotamine or yohimbine does not reverse but only decreases the pressor action. Reversal of pressor action such as occurs with adrenaline is dependent on the vaso-dilator action being sufficiently powerful.

W. O. KERMACK.

Absorption of *Digitalis* preparations from the intestine. A. VON NYÁRY (Arch. exp. Path. Pharm., 1932, 165, 432—442).—Digitoxin is absorbed from the intestine of the cat twice as rapidly as digiclarin or strophanthin and three times as rapidly as *Digitalis* infusion. Digitonin or saponin antagonises the absorption of digiclarin and digitoxin but accelerates that of strophanthin. The residual, saponin-containing, "ballast-substance" from the purification of the digiclarin exhibits a marked inhibitory action on the absorption of digiclarin, digitoxin, and strophanthin.

F. O. HOWITT.

Fate of salicylic acid introduced into the body. II. C. W. MYUNG (Folia Pharmacol. Japon., 1931, 12, No. 3, 428—433).—In normal rabbits the blood-salicylic acid is max. 1 hr. after subcutaneous injection

of Na salicylate; in 24 hr. it is zero. After previous treatment with HCl or NaHCO₃ the max. was reached in 2—4 hr. or 20 min., respectively.

CHEMICAL ABSTRACTS.

Currosaponin. C. A. SAGASTUME and L. P. PONCE (Semana méd., 1931, II, 227—228).—The hæmolytic power of the saponin of *Colletia cruciata*, Gill and Hook, is destroyed by large, but not by small, doses of sugars. The min. lethal subcutaneous dose for rats is 0.6 mg. per g. Certain bacteria destroy the hæmolytic power of saponin solutions, leaving the toxicity and foam-producing qualities unchanged; hence hæmolytic tests for the detection of saponin in beverages may be untrustworthy.

CHEMICAL ABSTRACTS.

Mechanism of the uric acid excretory action of cinchophen preparations. I, II. P. H. RI (Folia Pharmacol. Japon., 1931, 13, No. 1, 1—12, 13—21).—I. Increase in urinary and blood-uric acid in dogs follows subcutaneous injection of erycon (2-*p*-methoxyphenylquinoline-4-carboxylic acid). The intestine or liver forms uric acid faster than muscle, and muscle faster than the brain. The uric acid contents of portal and femoral blood, liver, etc. are compared.

II. Subcutaneous injection of erycon produces a greater difference in concn. between hepatic and portal blood in splachnectomised than in normal rabbits. Vagotomy does not depress the action of erycon on the transport of uric acid retained in the liver.

CHEMICAL ABSTRACTS.

Pharmacology of thebaine and its derivatives. II. **Influence on nitrogen metabolism.** Y. TAKEUCHI (Sei-i-kwai Med. J., 1930, 49, No. 9, 74—87).—Quant. changes in blood- and urinary N exhibited by rabbits on subcutaneous injection of thebaine, dihydrothebaine, oxycodone, and dihydrohydroxycodone hydrochlorides are recorded.

CHEMICAL ABSTRACTS.

Effect of India ink and of tolylenediamine on the augmenting properties of bile salts on glycogen synthesis by the liver. S. FUJITA (Arb. Med. Univ. Okayama, 1931, 2, 557—565).—Small amounts of C₇H₆(NH₂)₂ are slightly synergistic, but larger amounts, or India ink, are antagonistic, to the augmenting influence of bile salts on the glycogen-synthesising property of the liver.

CHEMICAL ABSTRACTS.

Pharmacological actions of some alkyl derivatives of harmol. II. Propylharmol. G. K. ELPHICK and J. A. GUNN. III. Butylharmol. J. A. GUNN and M. H. MACKEITH. IV. Amylharmol. V. Nonylharmol. G. K. ELPHICK and J. A. GUNN (Quart. J. Pharm., 1932, 5, 37—47, 48—55, 56—62, 63—71).—With increasing length of side-chain, general symptoms in the frog appear more slowly; increased motor excitability in mammals is decreased, with correspondingly earlier onset of paralysis; contracture of voluntary muscle occurs less readily; stimulation of uterus decreases and inhibition becomes more marked. In small doses, all except the Bu compound cause pressor effects, and in larger doses all produce a fall in blood-pressure. Respiration is depressed in the order Pr > Et, whilst Bu, amyl, and nonyl compounds always cause acceleration, nonyl being much slower in action than the

others. Mammalian coronaries are dilated and heart-muscle is depressed in the order $\text{amyl} \gg \text{Pr} > \text{Et} > \text{Bu} \gg \text{nonyl}$. The isolated intestine is relaxed by moderate doses of amyl, Bu, Pr, Et (Pr > Et) and stimulated by minute doses. Nonylharmol is by far the most toxic to protozoa and slowest in action.

J. B. BATEMAN.

Pharmacological action of new choline derivatives in relation to their chemical constitution. W. F. VON OETTINGEN and D. F. EVELETH (J. Pharm. Exp. Ther., 1932, 44, 465—477).—Substitution of the alcoholic OH group by Cl or the quaternary trimethylammonium chloride radical reinforces the characteristic choline actions, whereas substitution by NH_2 - and NHMe -groups increases the depressant action on muscular tissue; hence it follows that the $\cdot\text{NMe}_3 \cdot \text{C}_2\text{H}_4 \cdot$ nucleus is pharmacologically the essential part of the choline molecule. H. DAVSON.

Neutralisation of toxic properties of strychnine sulphate. A. C. MARIE (Ann. Inst. Pasteur, 1932, 48, 449—456).— KMnO_4 will neutralise the toxicity of about an equal wt. of strychnine sulphate. Neither adrenaline nor blood alone shows any effect, but together they detoxicate strychnine sulphate; the blood may be replaced by bile. The alkaloid is non-toxic even when extracted from the mixture by Et_2O , but regains its toxicity on reduction by $\text{Na}_2\text{S}_2\text{O}_4$. The effect is due to a preferential oxidation of strychnine in presence of adrenaline.

P. G. MARSHALL.

Spermicidal activity of quinones and quinols. J. M. GULLAND (Biochem. J., 1932, 26, 32—45).—The toxicities to spermatozoa of many phenols, quinols, and *o*- and *p*-quinones have been determined. The greater toxicity of *p*-quinones and quinols is related to their greater chemical reactivity. Introduction of an alkyl group into *p*-benzoquinone enhances activity, but further alkylation decreases the toxicity. Aromatic *o*-hydroxyaldehydes are more spermicidal than the *m*- or *p*-derivatives. The following are new: 2:5-dihydroxyphenyl *Pr* ketone, m. p. 87—89°; 2:5-dihydroxybutylbenzene, m. p. 89°; butyl-1:4-benzoquinone, m. p. 32°. A. COHEN.

Calcium therapy. M. BUFANO (Clin. méd., 1928, No. 6; Rev. sud-amer. endocrinol., 1931, 14, 705—706).—After intramuscular injection of CaCl_2 (0.15 g.) the blood-Ca is increased for 24 hr.; the increase in K is slower. The use of Ca gluconate does not always cause higher calcæmia; the ratio K:Ca is always low.

CHEMICAL ABSTRACTS.

Formation of wheals. IV. Influences of calcium concentration on histamine wheals. W. K. WEAVER, H. L. ALEXANDER, and F. S. McCONNELL (J. Clin. Invest., 1932, 11, 195—209).—Ingestion of NH_4Cl decreases, and of NaHCO_3 increases, histamine wheals; an explanation involves change in Ca concn.

CHEMICAL ABSTRACTS.

Cadmium poisoning. I. History of cadmium poisoning and uses of cadmium. L. PRODAM (J. Ind. Hygiene, 1932, 14, 132—155).

Effect of phosphate and hydrogen carbonate buffers on ionisation of calcium salts in physiological salt solutions. W. F. VON OETTINGEN and R. E. PICKETT (J. Pharm. Exp. Ther., 1932, 44,

435—443).—Ca ions are determined by measuring their effect on a drop of castor oil floating on H_2O in presence of soap. Concn. of the order of 0.03% of NaHCO_3 and 0.008—0.048% phosphate buffers cause association of the Ca ions. The effect of phosphate buffers is modified by the addition of 0.008—0.015% of NaHCO_3 . H. DAVSON.

Influence of light-rays on the total cholesterol content of the skin. S. KAWAGUCHI (J. Biochem. Japan, 1932, 15, 111—114).—Artificial irradiation of the rabbit results in an increase of cholesterol and its esters in the skin. The H_2O content is also increased. F. O. HOWITT.

Synthesising action of enzymes. R. AMMON (Angew. Chem., 1932, 45, 357—359).—A review.

Laws of combination of enzymes with substrates. H. FISCHGOLD and R. AMMON (Biochem. Z., 1932, 247, 338—353).—All enzymic processes which can be explained on the basis of the law of mass action (Michaelis and Menten) can also be based on Langmuir's adsorption theory. The lack of conformity to the theories at high substrate concn. is a consequence of elimination of H_2O from the surface of reaction. The reversal of the direction of optical rotation produced by some esterases when the concn. of the substrate is high may be due, if the adsorption theory is assumed, to differing sensitivity of the two diastereoisomeric enzyme-substrate compounds, to the decreased concn. of H_2O in the region of reaction, or to alteration in the proportions of the two antipodes resulting from change in the concn. of the substrate. A third possibility is that the enzyme undergoes irreversible alteration when this concn. becomes high.

W. MCCARTNEY.

Determination of oxidase. T. HANAZAWA (Trans. Tottori Soc. Agric. Sci., 1931, 3, 187—194).—The neck of the flask containing the sample is provided with side-tubes and containers for *N*- NaOH (25 c.c.) and 1% pyrocatechol solution (10 c.c.) and with a mineral-oil manometer. The O_2 absorption for 100 c.c. of potato juice was about 40 mg.

CHEMICAL ABSTRACTS.

Milk-peroxidase. Preparation, properties, and action with hydrogen peroxide on metabolites. Determination of small amounts of hydrogen peroxide in complex mixtures. K. A. C. ELLIOTT (Biochem. J., 1932, 26, 10—24).—A crude concn. peroxidase free from catalase is obtained from milk by fractional pptn. with $(\text{NH}_4)_2\text{SO}_4$. The prep. loses activity very slowly at 0—5°, and is active between p_{H} 4 and 10. Thiol compounds interfere with peroxidase tests using benzidine, guaiacum, and *p*-phenylenediamine. H_2O_2 is determined by measuring the O_2 liberated by MnO_2 . Under conditions suitable for the complete oxidation of NaNO_2 by H_2O_2 in the presence of peroxidase, no oxidation of formate, acetate, oleate, stearate, triolein, EtOH, glucose, glycerol, MeCHO, β -hydroxybutyrate, lactate, glycine, phenylalanine, or histidine was observed, whilst tyrosine and tryptophan were oxidised to coloured products. Dihydroxyacetone and phenylglyoxal were oxidised by dil. H_2O_2 without peroxidase. A. COHEN.

Accelerating action of uric acid on the xanthine-oxidase system. D. C. HARRISON (Biochem. J., 1932, 26, 472—475).—The inhibiting action of uric acid on the oxidation of hypoxanthine in presence of xanthine-oxidase and methylene-blue may be converted into an acceleration either by increasing the hypoxanthine or decreasing the enzyme concn. The accelerating effect appears to be due to the replacement on the enzyme surface of the inhibitor hypoxanthine by the less powerful inhibitor uric acid.

S. S. ZILVA.

Tyrosinase and pseudo-peroxidase. S. BERENSTEIN (Arch. Sci. phys. nat., 1932, [v], 14, 24—54).—The various types of oxidising enzymes are discussed and classified. Pseudo-peroxidase, a dehydrogenase, occurs in *Cyperus esculentus*, L., and other plants, but is isolated from these sources only with difficulty. Sweet almonds, however, readily yield the enzyme on aq. extraction. The extract is pptd. by EtOH, yielding an active ppt. In presence of NaHCO₃ and H₂O₂ the enzyme forms a red pigment from *p*-cresol. The additional presence of an NH₂-acid, indole, or phloroglucinol results in the formation of characteristic pigments. The pigment yielded by an NH₂-acid is identical with that produced by tyrosinase in presence of the NH₂-acid; the presence of H₂O₂ is essential for pseudo-peroxidase to react in this way. The accelerating influence of H₂O₂ on the *p*-cresol-tyrosinase reaction is not confirmed (cf. A., 1930, 1474). "Cresol-azure," the blue pigment from *p*-cresol, is prepared by the action of potato-oxidase in presence of glycine; it is identical with the product from 3:4-toluquinone (A., 1911, i, 728) and glycine. Solutions of this pigment show absorption bands at 530—610, 588, and 555 m μ . The pigments from phloroglucinol ("cresol-rubin") and indole ("indocresol") are similarly synthesised and examined.

F. O. HOWITT.

α - and β -Amylase in malt and barley. E. WALDSCHMIDT-LEITZ, M. REICHEL, and A. PURR (Naturwiss., 1932, 20, 254).—Treatment of a green-malt extract at p_H 3.8 with Al₂O₃ gives in the mother-liquor the pure α -component, whilst in the alkaline washings of the adsorbate the β is found. In this method they may be separated from the natural activator of amylase, *amylokinase*. Barley contains both α - and β -amylase, the α being in its inactive form; α -amylase seems necessary for the rapid conversion of starch into sugars.

H. DAVSON.

Action of cellulase and hemicellulase on plant materials *in vitro*. K. SILBERSCHMIDT (M \ddot{u} nch. med. Woch., 1931, 78, 1819—1824; Chem. Zentr., 1931, ii, 3499).—Loss of sensitivity to cellulose dyes is followed by loss of sensitivity to pectin dyes, the effects being parallel with the softening of the cell membrane.

A. A. ELDRIDGE.

Dilatometric investigation of enzymic processes. II. Di- and tri-saccharides. P. RONA, N. NEUENSCHWANDER-LEMMER, and H. FISCHGOLD (Biochem. Z., 1932, 247, 257—274; cf. A., 1931, 983).—During the hydrolysis of lactose, cellobiose, and raffinose with enzymes (emulsin, invertase) and with dil. H₂SO₄, vol. decreases proportional to the changes in optical rotation and similar to those

previously found with sucrose and maltose are observed. When more conc. acids are employed with cellobiose and lactose the decreases in vol. differ from those found with enzymes and dil. acids, whilst with maltose and glucose there is a vol. increase irregular for the former, regular for the latter. The mutarotations of glucose, galactose, and fructose are accompanied by vol. changes related to the changes of form which occur during the process. In the case of glucose and galactose the vol. changes which accompany the complete change of one modification into the other are equal.

W. MCCARTNEY.

Action of the alkaloids and carbon monoxide on the enzymic activity of plants. M. PADOA (Nature, 1932, 129, 686).—The addition of small amounts of strychnine nitrate increases the amylase activity of barley during germination, and the activities of lipase, amylase, protease, and oxidase in castor-oil seeds germinating in H₂O, but not the enzymic extracts of seeds. *Ricinus* seedlings are improved by additions of strychnine nitrate and caffeine, but the latter is toxic towards barley, flax, and other plants. Small amounts of CO stop the assimilatory activity of green plants in light but not the respiration; CO slightly increases the lipase activity but decreases the amylase activity of barley and of *Ricinus*. Wheat, lupins, and peas germinate in an atm. rich in CO, cabbage and hemp germinate with difficulty, whilst flax and tomato fail. N assimilation in leguminous plants appears to be due, but not exclusively, to the stimulating action of N bacteria; it is also related to enzymic activities latent in the plants.

L. S. THEOBALD.

Directive influences in biological systems. I. Specificities of lipase actions. K. G. FALK (J. Biol. Chem., 1932, 96, 53—71).—The action of pancreatic lipase on various simple esters alone and in presence of inactive proteins or of lipolytically active normal tissue- and tumour-extracts was investigated. In addition to the protective action by the added material there occurred interaction which resulted in selectively increasing certain of the hydrolyses. It is suggested that lipase or ester-hydrolysing actions are due to a definite grouping on the enzyme and that the sp. action of the added tissue extracts or proteins is due to certain characteristics of the added substance.

F. O. HOWITT.

Isolation of asparagine from an enzymic digest of edestin. M. DAMODARAN (Biochem. J., 1932, 26, 235—247).—Edestin was digested by the successive action of pepsin, trypsin, and yeast-di-peptidase with only slight splitting of amide-N, and asparagine was isolated from the digest. The presence of glutamine was also indicated by the method of Chibnall and Westall (cf. this vol., 660).

A. COHEN.

Proteolytic enzymes of the pancreas and intestine. (MLLE.) E. LE BRETON (Bull. Soc. Chim. biol., 1932, 14, 417—506).—A lecture.

Proteolytic degradation of crystalline urease. E. WALDSCHMIDT-LEITZ and F. STEIGERWALDT (Z. physiol. Chem., 1932, 206, 133—136).—It is reaffirmed that by the action of proteinase up to 80% of the substance in cryst. urease precipitable by

sulphosalicylic acid is destroyed without affecting the urease activity (cf. Sumner and Kirk, this vol., 544).

J. H. BIRKINSHAW.

Crystalline urease. Preparation of meal from jack-beans. J. S. KIRK and J. B. SUMNER (Ind. Eng. Chem., 1932, 24, 454—455).—A special grinder is described.

P. G. MARSHALL.

Uricase and its action. V. Ox-kidney uricase. R. TRUSZKOWSKI (Biochem. J., 1932, 26, 285—291).—Ox-kidney uricase suspensions do not yield fractions of different activity on sedimentation. Both medullary and cortical tissues are active, the action of the latter being, however, about 25% greater than that of the former. Uricase is irreversibly inactivated in solutions of p_{H} 2—6.56, but not of p_{H} 7.59, by neutral solutions of KCN, I (0.01—0.1N), H_2O_2 , FeSO_4 , and HgCl_2 , but not by CuSO_4 . The enzyme is completely inactivated by heating for 5 min. above 70° and almost completely at 70°, partly at 60°, and not at all at 50° or less. KCN completely inhibits uricolysis by ox-kidney uricase, whilst $\text{Na}_4\text{P}_2\text{O}_7$ has no effect. Dog, rabbit, and cat kidneys do not contain uricase.

S. S. ZILVA.

Action of phosphatase on various substrates. Y. IMANISHI (Biochem. Z., 1932, 247, 406—417).—Na fructosemonophosphate is hydrolysed to the extent of 80—97% (according to experimental conditions) by phosphatase from *Aspergillus oryzae* and from top and bottom yeast. K diphenylorthophosphate is hydrolysed by takaphosphatase to the extent of 44.5—62.0% and by phosphatase of animal origin (rabbit kidney and liver) to the extent of 35—63%.

W. MCCARTNEY.

Phospho-monoesterase and -diesterase. S. UZAWA (J. Biochem. Japan, 1932, 15, 19—28).—Adsorption methods applied to aq. extracts of rice-bran or to solutions of takadiastase yield an enzyme solution which hydrolyses mono-esters but not di-esters of H_3PO_4 . The venom of the snake *Trimeresurus flavoviridis* contains a di-esterase with a p_{H} optimum of 8.6. This enzyme admixed with the mono-esterase from takadiastase hydrolyses completely a di-ester of H_3PO_4 , the optimum being at p_{H} 5.6.

F. O. HOWITT.

Phosphatase from bran. I, II. S. UZAWA (J. Biochem. Japan, 1932, 15, 1—10, 11—17).—I. Rice-bran is extracted with H_2O , the extract dialysed, treated with kaolin, and the adsorption complex eluted with phosphate buffer to yield a solution of the enzyme which, following dialysis for removal of PO_4''' , is further purified by electro-dialysis. This solution contains a phosphatase which hydrolyses various types of mono-esters of H_3PO_4 at an optimum reaction of p_{H} 5.4—5.6. Hence there exist three types of monophosphatases with p_{H} optima at 3, 5.5, and 9, respectively (cf. A., 1929, 847; 1930, 372).

II. The solution also contains an enzyme hydrolysing di-esters of H_3PO_4 with p_{H} optima varying from 3.0 to 5.1 according to the concn. of the substrate.

F. O. HOWITT.

Hydrolysis of glucose-sulphuric acid and sucrose-sulphuric acid by phosphatase from bacteria. B. TANKÓ (Biochem. Z., 1932, 247, 486—

490).—Chondrosulphatase from bacteria hydrolyses these acids to the extents of 53 and 29%, respectively.

W. MCCARTNEY.

Dehydrogenating enzymes. H. WIELAND (Helv. Chim. Acta, 1932, 15, 521—532).—A lecture.

H. A. PIGGOTT.

Preparation of succinodihydrogenase free from fumarase. N. ALWALL and J. LEHMANN (Skand. Arch. Physiol., 1931, 61, 159—160; Chem. Zentr., 1931, ii, 3498).—Fumarase is not decomposed by heating at 50°. Fumarase can be washed out of muscle, whereas succinodihydrogenase remains and can be extracted with phosphate.

A. A. ELDRIDGE.

Arginase. VII. Activation and inhibition experiments. S. EDLBACHER, J. KRAUS, and G. WALTER. **VIII. Thyroxine and arginine metabolism.** S. EDLBACHER and B. SCHULER (Z. physiol. Chem., 1932, 206, 65—77, 78—83; cf. A., 1931, 393).—VII. Arginase changes its solubility in COMe_2 or EtOH preps., becoming almost insol. in glycerol and H_2O , sol. in buffers of p_{H} 6.4—9.4. Liver COMe_2 extract evaporated in vac. does not activate arginase. HCN, cysteine, and glutathione inhibit arginase at neutrality even at 0.001M. At p_{H} 9.4 cysteine produces weak activation. The statement that arginase acts only in presence of natural activator (glutathione etc.) was not confirmed. O_2 inactivates arginase at 40°, particularly at alkaline reaction, N_2 only slightly; such a partly inactivated product is inhibited by cysteine at p_{H} 6.8 in the same way as native arginase, but there is no reactivation at p_{H} 9.4. Frothing produces strong inactivation.

VIII. Injection of arginine into guinea-pigs increases the arginase val. of the muscle (fourfold) and kidneys; the max. vals. are attained in 5 hr. If thyroxine is injected 1 hr. before the arginine, no increase of muscle-arginase is observed. Surviving cat's liver perfused with erythrocytes in Ringer solution hydrolyses only 60—70% of the amount of arginine hydrolysed without thyroxine.

J. H. BIRKINSHAW.

Iron in relation to tyrosinase. C. E. M. PUGH (Biochem. J., 1932, 26, 106—117).—The activity of tyrosinase preps. from mealworms and fungi, as free from extraneous Fe as possible, is not related to the Fe content of the enzyme prep. There is no evidence, however, that tyrosinase does not contain Fe. The hastening of the coloration of tyrosine and *p*-cresol by tyrosinase on addition of Fe'' salts indicates the formation of H_2O_2 . The oxidation of phenols by H_2O_2 and Fe'' salts is not as sp. as the tyrosinase action. Dialysis causes loss of activity of tyrosinase which is prevented by dialysing into a medium at p_{H} 8.5.

A. COHEN.

Properties of glyoxalase. J. O. GERŠAVIČIUS (Biochem. J., 1932, 26, 155—161).—PhMe inhibits the action of glyoxalase. Borate buffer has little effect, but phosphate and diethylbarbiturate have increasing inhibiting effect. The optimum p_{H} for glyoxalase is 6—7.

A. COHEN.

Baicalinase, an enzyme which hydrolyses flavone glycuronides. I. T. MIWA (Acta Phytochim., 1932, 6, 155—175).—Baicalinase (I) (A., 1931,

493; modified prep.) hydrolyses baicalin (II) and scutellarin (III), but not rutin, robinin, myricitrin, k mferitrin, acaciin, salicin, or amygdalin. It is thus different from emulsin, takadiastase, and rhamno-diastase, which do not hydrolyse (II) or (III). Menthol-glycuronic acid was not hydrolysed by Kahlbaum's emulsin nor by (I). A table of C_u equivs. is given for determination of glycuronic acid [K salt does not mutarotate in H_2O (cf. A., 1929, 541)] by Bertrand's method. (I) is most active at p_H 5.9—6.0.

R. S. CAHN.

Plastein. S. J. FOLLEY (Biochem. J., 1932, 26, 99—105).—The mol. wt. of plastein, determined by the ultra-centrifugal method, is <1000. The amide-N is less, and the NH_2 -acid-N greater, than in the parent ovalbumin. The $PhNCO$ derivative yields two fractions with equivs. of the same order as that of proteose. Plastein is not regarded as a product of enzyme synthesis.

A. COHEN.

Respiratory processes in pea and cereal seeds. IX. R le of boiled yeast-juice. Oxidised carotene as hydrogen acceptor. A. FODOR and L. FRANKENTHAL (Biochem. Z., 1932, 246, 414—430).—The dehydrogenating activities of various meals are studied in relation to various hydrogen acceptors. Boiled yeast juice is essential to the reaction in some cases, and under certain conditions methylglyoxal and also oxidised carotene retard the process. Their effect on the respiration is also studied.

H. W. DUDLEY.

Selective fermentation of glucose and fructose by yeast. E. R. DAWSON (Biochem. J., 1931, 26, 531—535).—Theoretical.

S. S. ZILVA.

Mechanism of the formation of organic acids by mould fungi. I. Action of *Aspergillus niger* on sodium hexosediphosphate in the presence of toluene. A. J. SUTHERS and T. K. WALKER (Biochem. J., 1932, 26, 317—322).—*A. niger* forms methylglyoxal from Na hexosediphosphate.

S. S. ZILVA.

Effect of acid on the growth of moulds. A. JURACEC (Bull. Acad. Sci. Roumaine, 1932, 15, 47—50).—The optimum reaction for the germination of spores of *Aspergillus niger* in Raulin's medium is p_H 3.45. The reaction is varied by addition of tartaric acid or K_2CO_3 . When tartaric acid is replaced by H_3PO_4 the optimum p_H is 3.7. A $p_H > 8$ inhibits growth.

P. G. MARSHALL.

Relation between the sugars of *Aspergillus niger* and those serving as nutrients. OBATON (Compt. rend. Soc. Biol., 1930, 105, 673—674; Chem. Zentr., 1931, ii, 3501).—Addition of glucose to the nutrient solution leads to a high yield of trehalose in the mycelium; mannitol is formed to only a small extent. With invert sugar or fructose the reverse holds.

A. A. ELDRIDGE.

Metabolic physiology of *Aspergillus oryzae*. IV. Utilisation of various carbon compounds [for growth and respiration] of moulds. H. TAMIYA (Acta Phytochim., 1932, 6, 1—129; cf. A., 1929, 958).—By the use of a semi-quant. technique, described in detail, it is shown that *A. oryzae* grown from cultures can utilise 51 (mostly alcohols and

acids) out of 123 org. compounds examined for growth and respiration, and 8 for respiration only, whilst 17 were without effect and 47 were deleterious. When grown from spores, the mould utilises only 47 for good growth, 7 for slight growth, and 69 not at all. Certain groups, e.g., CO, CHO, ether, inhibited growth (in the concns. used), but in general the presence of one sp. group was not sufficient for growth. The two series of experiments gave approx. parallel results for different substances. *A. oryzae* utilises many sugars and $AcCO_2H$, but not alcohols, acids, aldehydes, ketones, or ethers, for anaerobic fermentation, which is similar in nature to fermentation by yeast. Kojic acid is formed from many compounds containing from 3 to 6 C atoms. From a comparison of the formul e of the compounds examined it is concluded that certain pairs of groups [e.g., $CHMe(OH)$, $\cdot CH\cdot C(OH)\cdot$, $\cdot CH_2(OH)\cdot CH_2\cdot$, etc. (termed "chief radicals")] must be present in an utilisable compound, joined at least once (in a ring or a straight chain) to another group (termed "residual radical"), such that β -degradation does not lead to fission of the "chief radical." Fission of di- and poly-saccharides and of glucosides precedes their utilisation by the mould, and the nascent fission products can usually be utilised better than the preformed substance.

R. S. CAHN.

Biochemistry of micro-organisms. Puberulic acid, $C_8H_6O_6$, and an acid, $C_8H_4O_6$, new products of the metabolism of glucose by *Penicillium puberulum*, Bainier, and *Penicillium aurantio-virens*, Biourge. Certain dihydroxybenzenedicarboxylic acids. J. H. BIRKINSHAW and H. RAISTRICK (Biochem. J., 1932, 26, 441—453).—Each of these acids is produced by *P. puberulum* and *P. aurantio-virens* when grown in a synthetic medium containing glucose as sole source of C. Puberulic acid (I), $C_8H_6O_6$, m. p. 316° (decomp.) (Ac_2 derivative, m. p. 212° ; Me , m. p. 272 — 276° , decomp. 320 — 330° , Me_2 , m. p. 271 — 272° , and Me_4 , m. p. 112 — 113° , derivatives; diacetyldimethyl derivative, m. p. 102°), and the acid $C_8H_4O_6$ (II), m. p. 296° (decomp.), are pptd. from the neutralised filtered metabolic solutions as the Ni salts. The acids are separated by treating the mixed salts with Ac_2O and $NaOAc$; (II) is pptd., whilst (I) remains in solution as the Ac_2 compound. (I) is probably a dihydroxybenzenedicarboxylic acid. (I) and (II) may form an oxidation-reduction system.

S. S. ZILVA.

Supposed production of maclurin from acacatechin. M. HEALEY (Biochem. J., 1932, 26, 388—391).—No maclurin is formed from Gambier catechin or acacatechin by the action of *Penicillium solitum* (cf. Hazleton and Nierenstein, A., 1924, i, 1218).

S. S. ZILVA.

Production of acetoin by Linder's *Thermobacterium mobile*. B. TANK  (Biochem. Z., 1932, 247, 482—485).—In solutions containing glucose (or glucose and sucrose) and $MeCHO$ the bacterium produces acetoin in yields equiv. to about 40% or more of the aldehyde originally present.

W. MCCARTNEY.

Factors influencing the formation of products in the thermophilic fermentation of cellulose.

W. B. SARLES, E. B. FRED, and W. H. PETERSEN (Zentr. Bakt. Par., 1932, II, 85, 401—415).—Differences in acid production by crude and purified cultures under varied cultural conditions are recorded. A pure culture produced volatile acids consisting of 71% of AcOH and 29% of butyric acid. A. G. POLLARD.

Biochemistry of light-producing bacteria. I. Influence of sodium and potassium chlorides and bromides on the generation of light by *Photobacillus radians*. F. FUHRMANN (Monatsh., 1932, 60, 69—105).—The isolation of *P. radians* from North Sea codfish or haddock and its characterisation are described; it can develop under anaerobic conditions but glows only in presence of O₂, best at p_H 7.1—7.4. The effect on growth of the bacteria and the amount of light produced of NaCl, NaBr, KCl, and KBr is studied in presence and absence of glycerol in a fish bouillon-peptone medium. With the same cation, which may be either Na⁺ or K⁺, the effect on the glow produced by the anions Cl⁻ and Br⁻ differs, and they cannot replace each other in isotonic solution; the same is true of the cations combined with the same anion. KCl and KBr tend to cause agglomeration of the individual cells, an effect observed with Na salts only in high concn. The production of light and the multiplication of cells do not seem to be related. H. A. PIGGOTT.

Influence of the medium on production of bacterial gelatinase. R. B. HAINES (Biochem. J., 1932, 26, 323—336; cf. this vol., 197).—The change in viscosity of a mixture of gelatin and sterile centrifugate from the medium in which the organism (*proteus* or *Pseudomonas*) had been grown indicated that a certain amount of gelatinase is present whatever the medium used, providing adequate growth occurred. In a synthetic medium containing no Mg or Ca salts no single NH₂-acid is markedly superior to any other or to NH₄Cl in its effect on gelatinase production, although rather better growth is obtained with some than with others. In all cases salts of Ca and Mg together greatly stimulate the production of gelatinase. In some cases salts of Mg alone while stimulating growth partly inhibit gelatinase formation. Salts of Ca alone have little or no growth-stimulating action, but in most cases greatly stimulate gelatinase production. In a medium containing NH₄Cl, glucose, or phosphates together with salts of Ca and Mg, gelatinase is produced to the same extent as in broth. S. S. ZILVA.

Physiology of amoeboid movement. VIII. Action of certain non-electrolytes. Isoelectric point of the proteins of a marine amoeba. C. F. A. PANTIN (J. Exp. Biol., 1931, 8, 365—378).—Movement in 1.05*M*-sucrose, -glucose, -glycerol, or -urea was studied. The isoelectric point is p_H 4.6—5.

CHEMICAL ABSTRACTS.

(i) Presence of a principle lysing Yersin's bacillus in the blood of a plague convalescent. M. ADVIER. (ii) Existence in a bubo of a plague convalescent of an agent producing transmissible lysis, apart from its presence in the intestine. R. PONS and C. DURIEUX (Compt. rend., 1932, 194, 1397—1399, 1399—1400).—(i) From the serum of a

convalescent recovering from plague a bacteriophage has been obtained which produces transmissible lysis in cultures of Yersin's bacillus (*B. pestis*).

(ii) The bacteriophage was also isolated from a bubo. W. O. KERMAK.

***Bacillus coagulans*.** W. B. SARLES and B. W. HAMMER (J. Bact., 1932, 23, 301—314).—Evaporated milk coagulated by *B. coagulans* contained abnormally high proportions of total and volatile acids. The latter consisted mainly of AcOH and EtCO₂H. The non-volatile acid was *d*-lactic acid. Coagulated evaporated milk shows no evidence of proteolysis, but in coagulated skim-milk there was an increase in sol. and NH₂-N. Gas from tins of normal or coagulated, evaporated milk contained no O₂, but with coagulated samples the CO₂ content was above normal. A. G. POLLARD.

Reaction regulators for bacteriological cultures. (a) A. BERTHELOT. (b) A. BERTHELOT and G. AMOUREUX. (c) A. BERTHELOT, F. VAN DEINSE, and G. AMOUREUX (Bull. Soc. Chim. biol., 1932, 14, 280—285, 286—289, 290—293).—(a) (b) The p_H of cultures of *B. aminophilus* on meat peptone media with and without addition of glucose and each containing quantities of the K or Na salt of one of the following acids, HCO₂H, AcOH, EtCO₂H, pyruvic, lactic, malonic, butyric, malic, fumaric, etc., is found to change at definite rates according to the acid used and as the media contain or do not contain glucose. It is suggested therefore that such acids can be used as buffers.

(c) The Na salts of acyclic acids known to be attacked by *B. tuberculosis* can be used to regulate the p_H of cultures of this bacillus, but the choice of the acid depends on the nature of the medium.

A. LAWSON.

Origin of acetylmethylcarbinol in the degradation of sucrose by *B. subtilis*. LAFON (Bull. Soc. Chim. biol., 1932, 14, 263—271).—In the products of fermentation of both glucose and fructose by *B. subtilis*, acetylmethylcarbinol is formed. Using glucose as substrate, negative results attended attempts to isolate pyruvic acid and MeCHO in the production of acetylmethylcarbinol, nor could the last-named substance be isolated using pyruvic acid and MeCHO as substrate. *B. subtilis*, unlike yeast, attacks MeCHO very slowly. It is suggested that the production of acetylmethylcarbinol by *B. subtilis* from glycerol is due to the intermediate synthesis of a hexose from which it is then produced directly.

A. LAWSON.

Relation of p_H to the absorption of dyes by bacteria. S. J. FRENCH and W. H. WRIGHT (Proc. Indiana Acad. Sci., 1931, 40, 175—177).—*Pseudomonas tumefaciens* and *Radiobacter*, when grown in presence of Congo-red, did not (as Stearn supposes) adsorb acid dyes in media of low p_H and basic dyes in those of high p_H , possibly owing to the amphoteric nature of Congo-red. CHEMICAL ABSTRACTS.

Influence of carbohydrates on the pigment production of *Azotobacter*. S. ARAKAWA (Tottori Agric. Coll. Sci. Papers (10th Anniv.), 24—31; Proc. Internat. Soc. Soil Sci., 1932, 7, 21—22).—Pigmentation of *A. chroococcum* occurred in simple media

containing raffinose, inulin, dextrin, or starch. *A. vinelandii* produced pigment in glycerol media but not in those containing polysaccharides. Both organisms showed pigmentation in 1% KNO_3 media containing glucose, fructose, maltose, sucrose, or mannitol. KNO_3 as a N-source intensified pigmentation.

A. G. POLLARD.

Nodule bacteria and production of phosphatides in *Soja hispida*. B. REWALD and W. RIEDE (Biochem. Z., 1932, 247, 424—428).—The phosphatide and oil contents of soya beans and plants are not affected at any stage of growth by the presence or absence of nodule bacteria, although these cause increase in the protein content. W. McCARTNEY.

Biochemical characters of human and animal strains of hæmolytic streptococci. P. R. EDWARDS (J. Bact., 1932, 23, 259—266).—Animal strains produce greater acidity in glucose media than do human strains, and are further differentiated by the production of acid from sorbitol and failure to ferment trehalose. Human strains ferment trehalose but do not attack sorbitol.

A. G. POLLARD.

Atypical (slow) lactose-fermenting *B. coli*. F. S. JONES, M. ORCUTT, and R. B. LITTLE (J. Bact., 1932, 23, 267—279).—During the fermentation of lactose by colon bacilli from cow fæces, there is a phase in which the sugar is utilised without acid production.

A. G. POLLARD.

Growth of *Aspergillus versicolor* on higher paraffins. S. J. HOPKINS and A. C. CHIBNALL (Biochem. J., 1932, 26, 133—142).—A strain of *A. versicolor* will grow on odd and even no. paraffins up to $\text{C}_{34}\text{H}_{70}$ as sole source of C. Apart from CO_2 and mycelium no metabolic products were obtained from a culture on $\text{C}_{27}\text{H}_{56}$. The mould grows well on the higher ketones but not on sec. alcohols. In the oxidation of paraffins, therefore, a ketone appears to be the initial product, which is further metabolised to shorter fatty acids.

A. COHEN.

Antibodies. IV. Carbohydrate content as a criterion of the suitability of a broth for the culture of pneumococci. G. MCGUIRE, E. VALENTINE, E. WHITNEY, and K. G. FALK (J. Bact., 1932, 23, 223—234).—Good broth should have 0.5 mg. of fermentable reducing substance per c.c. With the growth of the organism p_{H} changes in the medium correspond with acid produced from fermentable reducing substances.

A. G. POLLARD.

Bacterial metabolism. II. Glucose breakdown by pneumococcus variants and the effect of phosphate thereon. L. F. HEWITT (Biochem. J., 1932, 26, 464—471).—Of the glucose disappearing from cultures of pneumococci about 78% is recovered as lactic acid. The ratio of the latter to the broken-down glucose is unaffected by altering a variety of cultural conditions; this was previously observed in the case of hæmolytic streptococci. There is more glucose breakdown in growing cultures with certain forms of pneumococcus than with others. The presence of inorg. phosphate appears to play an essential part in bacterial growth and glucose breakdown and not merely that of a buffer salt.

S. S. ZILVA.

Rôle of the soluble specific substances in oral immunisation against pneumococcus types II and III. V. ROSS (J. Exp. Med., 1932, 55, 1—12).

CHEMICAL ABSTRACTS.

Fate of orally administered soluble specific substance of pneumococcus types I, II, and III. V. ROSS (J. Exp. Med., 1932, 55, 13—25).—The substance was excreted by rats largely in the fæces; none was detected in the serum or urine. The recovered polysaccharide of type I is active.

CHEMICAL ABSTRACTS.

Identity of the mechanisms of type-specific agglutinin and precipitation reactions with pneumococcus. T. FRANCIS (J. Exp. Med., 1932, 55, 55—62).—The essential mechanism is the same; the active agents are the capsular polysaccharides.

CHEMICAL ABSTRACTS.

Biology of the tubercle bacillus. II. Asparagine and glycerol metabolism of the tubercle bacillus. J. H. DINGLE and J. WEINZIRL (J. Bact., 1932, 23, 281—299).—The metabolism of virulent and avirulent strains of the organism was similar except that the former produced a final acidity and the latter a final alkalinity in the medium. The NH_3 content of the medium was greatest at the max. growth period and declined later. Alkalinity produced in media was probably not due to NH_3 . All the N of asparagine was utilised by the organism, the NH-N being more readily attacked than $\text{NH}_2\text{-N}$. Glycerol was almost completely utilised, and partial oxidation to org. acids did not occur.

A. G. POLLARD.

Specific carbohydrate of the tubercle bacillus. G. A. C. GOUGH (Biochem. J., 1932, 26, 248—254).—Mild hydrolysis of the carbohydrate with 2.5% H_2SO_4 or $\text{H}_2\text{C}_2\text{O}_4$ yields in addition to mannose, *d*-arabinose, and galactose, a mixture of acidic substances which have been investigated. Ca salts containing 2.5—10% Ca have been obtained by fractional pptn. Further hydrolysis destroys the acidity with production of mannose. Acetylation of the carbohydrate gives a H_2O -insol. substance converted by alkaline hydrolysis into the carbohydrate with the original pptg. power.

A. COHEN.

Bacterial metabolism. I. Lactic acid production by hæmolytic streptococci. L. F. HEWITT (Biochem. J., 1932, 26, 208—217).—Good cultures were obtained with a glucose-salt solution buffered with NaHCO_3 and containing 10% of meat broth. The lactic acid formed averaged about 75% of the glucose which disappeared under varying conditions. Matt virulent streptococci caused much more rapid breakdown of glucose than did glossy variants.

A. COHEN.

Decomposition of caseinogen by lactic streptococci under aerobic and anaerobic conditions. C. BARTHEL (Orla-Jensen Festschr., 1931, 60—62; Chem. Zentr., 1932, i, 153).—The yields of sol. and NH_2 -acid N were practically zero with *S. cremoris*, and little different with *S. lactis*.

A. A. ELDRIDGE.

Effect of various yeasts on the growth and physiological properties of lactic acid bacteria and moulds. O. K. PALLADINA and V. A. MASJUKEVITSCH (Orla-Jensen Festschr., 1931, 89—93; Chem. Zentr., 1932, i, 153).—Culture of lactic acid bacteria

with yeast is not a substitute for addition of yeast autolysate and does not promote the formation of acid. The growth of moulds is not markedly arrested by culturing with yeast; the proteolytic power of *Oidium lactis* in milk is even promoted and the production of acid in cream is arrested. A. A. ELDRIDGE.

Inhibition of bacterial lactic fermentation by the halogeno-aliphatic acids. L. GENEVOIS and T. NICOLAIEV (Compt. rend., 1932, 194, 1270—1271).—The lactic acid fermentation of bacteria is inhibited by bromo- and iodo-acetic acid and by their esters and homologues, as is the formation of lactic acid by muscle or EtOH by yeast. The inhibition is practically complete within several min. when the concn. of $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ or $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ is $N/2000$; the corresponding concns. for $\text{CHMeBr}\cdot\text{CO}_2\text{H}$ or $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$ are $N/100$, the respiration remaining unaffected for several hr. The inhibiting action is less marked in a medium poor than in one rich in phosphate. This supports the view that the effect of the acid is to inhibit the initial esterification of the phosphate. It is suggested that $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ or $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ may be used to prevent the souring of milk. W. O. KERMAK.

Respiratory processes of lactic acid bacteria. A. BERTHO and H. GLÜCK (Annalen, 1932, 494, 159—191).—Partly a more detailed account of work previously reviewed (A., 1931, 394). The following is new. Glucose is dehydrogenated by benzoquinone (I) in presence of *B. Delbrückii* or *B. acidophilus*; HCN ($M/625$ — $M/5000$) has no influence on the reaction, CO causes a slight activation, but $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ ($M/500$) has a considerable retarding action (more pronounced with *B. Delbrückii*). With methylene-blue (II) in place of (I), dehydrogenation is accelerated slightly by $M/500$ -HCN, retarded slightly by 0.05% ethylurethane and considerably by $M/500$ - $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$. The ratio of the activities of O_2 , (I), and (II) as acceptors is 1:4:2.5; the dehydrogenations with these substances are all catalysed by the same dehydrogenase. With mixtures of O_2 and (I), no O_2 is consumed in the initial stages of the reaction, but the amount absorbed increases with the disappearance of (I). With (II) + O_2 , a large (250%) increase in O_2 -uptake occurs initially; (II) probably functions as the H-acceptor, the resulting leuco-compound being re-oxidised by O_2 . The respiratory quotients of *B. acidophilus* and *B. Delbrückii* are 0.45—0.59 and 0.33, respectively, in contrast to the val. of 0.5 calc. from the equation $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O} + 12\text{O}_2 = 6\text{CO}_2 + 12\text{H}_2\text{O}_2$. The formation of lactic acid from glucose by *B. acidophilus* is completely inhibited by $M/500$ - $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$; respiration continues but is retarded. Dihydroxyacetone and glyceraldehyde are as efficient donators as glucose; AcCHO causes a diminished O_2 -consumption and H_2O_2 is never detected. Systems (such as the above) unaffected by HCN contain no Fe-porphyrin complexes. H. BURTON.

Vegetable peptone agars for quantitative work with *Lactobacillus acidophilus*. F. M. BACHMANN and W. D. FROST (Science, 1932, 75, 440—441). L. S. THEOBALD.

Propionic acid bacteria. I. Classification and nomenclature. C. H. WERKMAN and S. E.

KENDALL (Iowa State Coll. J. Sci., 1931, 6, No. 1, 17—32).—Nine species are recognised and their effects on 32 carbohydrates are recorded.

CHEMICAL ABSTRACTS.

Symbiosis of *Vibrio cholerae* with bacteriophage, and variations of its biological characteristics. W. DOORENBOS (Ann. Inst. Pasteur, 1932, 48, 457—469).—Details are given of the factors influencing the agglutination of sheep erythrocytes by cultures of *V. cholerae*. The variability of the hæmolytic power is due to the development of antibæmolysins in the older cultures. Modifications of most of the biological characteristics are dependent on the presence of bacteriophage. P. G. MARSHALL.

Bacterial antagonism and bacteriophage. A. GRATIA (Ann. Inst. Pasteur, 1932, 48, 413—437).—A strain of *B. coli* (V) was obtained which produced a toxin antagonistic to the growth of *B. coli* (ϕ) and to a smaller extent of *B. dysenteriae* (Shiga). The two strains are able to develop a resistance to the toxin as they can to bacteriophage. The active principle is pptd. by COMe_2 but inactivated by EtOH; unlike bacteriophage it is not destroyed by quinine hydrochloride. Other points of difference from bacteriophage are mentioned. P. G. MARSHALL.

Effects of various carbohydrates on production of diphtheria toxin with special reference to its flocculating titre and final p_{H} . E. L. HAZEN and G. HELLER (J. Bact., 1932, 23, 195—209).—Carbohydrates are essential to the production of toxic filtrates from *C. diphtheriae*. Glucose is more effective than maltose or glycerol in this respect. Dextrin is without action. The toxicity of the filtrates is largely dependent on the final p_{H} of the culture and is greater at p_{H} 7.1 than at the commonly accepted range (7.8—8.2). A. G. POLLARD.

Cryptotoxins. L. VELLUZ (J. Pharm. Chim., 1932, [viii], 15, 400—409).—A review.

Oligodynamic action of metals. A. J. MARKVOORT and K. T. WIERINGA (Chem. Weekblad, 1932, 29, 242—247).—The opposing dissolution and radiation theories regarding the bactericidal action of metals are discussed, and experiments on sterilisation by means of active Ag described. The Ag must first dissolve to be effective; some bacteria, especially those forming spores, are more resistant, and after repeated use the surface loses its sterilising power. The action is stronger if air has access to the solution, and with rise of temp. Dil. AgNO_3 solution exhibits properties similar to those of H_2O_3 which has been in contact with an active Ag surface. S. I. LEVY.

Action of ether and chloroform on *Actinomyces* of the asteroid type. J. DUCHÉ (Compt. rend., 1932, 194, 1509—1510).— Et_2O has little effect on *A. asteroides*, but CHCl_3 is toxic and removes a wax-like substance. W. O. KERMAK.

Natural and acquired resistance of certain strains of *Escherichia coli* to the bacteriostatic and germicidal effects of cations. E. K. BORMAN (J. Bact., 1932, 23, 315—329).—The bacteriostatic and germicidal efficiencies of Na, Mg, Ba, Ca, Fe, Cu, and Hg salts were of the same order for different strains of the organism. A. G. POLLARD.

Bactericidal activity of silver. G. LAKHOVSKY (Compt. rend., 1932, 194, 1200).—Polemical (cf. this vol., 546). W. O. KERMAK.

Bactericidal action of metals. P. LASSEUR, M. PIERRET, A. DUPAIX, G. MAGUITOT (Compt. rend., 1932, 194, 1401).—A reply to the above.

W. O. KERMAK.

Bactericidal action of silver on typhoid and colon bacilli. A. KLING (Compt. rend., 1932, 194, 1402—1404).—The bactericidal action of Ag on *B. coli* and typhoid bacilli is accounted for by the solubility of Ag in distilled H₂O. W. O. KERMAK.

Effect of the parathyroid hormone on the calcium content of human milk. F. ADAMCSIK and A. VON BEZNAK (Klin. Woch., 1931, 10, 2219—2220; Chem. Zentr., 1932, i, 407).—The Ca content of human milk is lowest in the morning. Injection of parathyroid hormone prevents the normal increase during the day. A. A. ELDRIDGE.

Hormothylin, the thyroid-stimulating hormone of the anterior pituitary lobe. H. PAAL (Klin. Woch., 1931, 10, 2172—2174; Chem. Zentr., 1932, i, 405).—“Prähormon” from urine of pregnancy partly protects mice against MeCN; this is attributed to the hormothylin component. The same agent is present in the anterior pituitary lobe. It is thermostable and may be administered orally.

A. A. ELDRIDGE.

Existence of an extra-pancreatic (or cellular) insulin in the dog after pancreatectomy. S. SOSKIN (Science, 1932, 75, 382).—A criticism (cf. Tuttle, New Eng. Med., 1932, 8, 206).

L. S. THEOBALD.

Insulin action of pure pancreatic secretion. F. L. SOLER (Rev. farm., 1931, 74, 1—7).—Pancreatic secretion, when injected intravenously, has an insulin effect. Gastric secretion increases the blood-sugar. CHEMICAL ABSTRACTS.

Effect of digestive fluids on the activity of insulin. A. A. SCHMIDT and K. TULJTSCHINSKAJA (Z. ges. exp. Med., 1931, 77, 58—66; Chem. Zentr., 1931, ii, 3223).—Gastric juice of the dog destroys insulin in 30 min. at 37°; the pancreatic juice does not completely inactivate it in 2 hr., whilst the intestinal fluids have scarcely any effect in 2 hr.

L. S. THEOBALD.

Cure of cachexia following hypophysectomy by administration of the growth hormone and its relation to the resulting adrenocortical repair. H. M. EVANS, K. MEYER, R. PENCHARZ, and M. E. SIMPSON (Science, 1932, 75, 442—443).—The growth rate of hypophysectomised rats receiving purified preps. of the growth hormone free from gonad-stimulating effect exceeded that of normal animals similarly treated. Prompt and uniform relief from the cachectic state follows administration of the growth hormone extracts, whilst the growth-free, gonad-stimulating hormone has no influence on the cachexia. The growth, but not the gonad, hormone also partly repairs the thyroids and the adrenals. Atrophy of the adrenals and the cachectic state are probably related causally. L. S. THEOBALD.

Oxytocic principle of the posterior lobe of pituitary gland. I. J. M. GULLAND and W. H. NEWTON (Biochem. J., 1932, 26, 337—348).—“Norit” adsorbs the oxytocic principle between p_H 1 and 13. The active substance can be eluted by glacial AcOH. The oxytocic activity which is recovered from the adsorbent when freshly-prepared partly-purified extracts are used varies from 50 to 75% of that of the same solution 3 weeks later even when kept at p_H 3 and 0°. In the case of the more mature solution the amount of activity recoverable is about 80% of the total. [H⁺] has no influence on the amount of activity adsorbed from fresh or more mature solutions. The most active prep. contains 225 international oxytocic units per mg.

S. S. ZILVA.

Pituitary. VIII. Relation of the pituitary gland to calcium metabolism and ovarian function in *Xenopus*. L. HOGBEN, E. CHARLES, and D. SLOME (J. Exp. Biol., 1931, 8, 345—354).—Removal of the pituitary or the anterior lobe alone lowers serum-Ca in *Xenopus laevis*.

CHEMICAL ABSTRACTS.

Œstrin. V. Mechanism of the conversion of trihydroxyœstrin into ketohydroxyœstrin. G. F. MARRIEN and G. A. D. HASLEWOOD (Biochem. J., 1932, 26, 25—31).—Trihydroxyœstrin (I), m. p. 279.5—280.5°, $[\alpha]_{5461} +41.9^\circ$ in C₅H₅N, +76° in EtOH, yields Butenandt's ketohydroxyœstrin (II), m. p. 242—246°, $[\alpha]_{5461} +188^\circ$ in EtOH, by dehydration with KHSO₄, and, with alkaline Me₂SO₄, a *Me ether* (III), m. p. 162.5—164°, $[\alpha]_{5461} +29.9^\circ$ in C₅H₅N, +65.3° in EtOH. (II) gives a *Me ether*, m. p. 164—167°, $[\alpha]_{5461} +171^\circ$ in CHCl₃, identical with the dehydration product of (III). The identity is confirmed by prep. of the *oxime*, m. p. 182—187°. H₂O is therefore eliminated between the non-acidic OH groups of (I) in its conversion into (II). The acidity of the latter is due to a phenolic OH group.

A. COHEN.

Active substances in testicles. G. PERITZ (Endokrinol., 1931, 9, 355—362; Chem. Zentr., 1932, i, 539).—Three active substances were found in the testicular extract of eunuchoid and castrated rats: (1) increasing the sugar combustion in the organism, (2) causing the development of secondary sexual characteristics, (3) providing for spermiogenesis. Possibly a fourth accelerates testicular growth.

A. A. ELDRIDGE.

Physiology and pathology of urinary excretion of prolan in children and adolescents. F. SCHÖRCHER (Klin. Woch., 1931, 10, 2221—2222; Chem. Zentr., 1932, i, 539).—The sexual hormone of the anterior lobe could not be found; all the hormone formed at this period appears to be utilised by the generative glands. A. A. ELDRIDGE.

Influence of the freshness of the testes and of desiccation of the testicular tissue on the yield of testicular hormone. V. KORENCHESKY, R. SCHALIT, and D. GRAETZ (Biochem. J., 1932, 26, 423—428).—Freshness plays an important part in the yield of the hormone. It is possible to dry at 37° testicular tissue without appreciably decreasing the yield of the hormone after boiling the tissue in H₂O

acidified with AcOH to p_{H} 4.6—4.8. Besides causing oxidation, the autolytic enzymes present in testicular tissue are probably the most destructive agents of the hormone.
S. S. ZILVA.

Assay of testicular hormone preparations. V. KORENCHESKY (Biochem. J., 1932, 26, 413—422).—The wt. of the prostate with the seminal vesicles of castrated rats injected and uninjected with the hormone is compared. An increase of 40% in wt. after 6 days' injection is taken as the criterion for the activity and strength of the prep.
S. S. ZILVA.

Influence of gonads on protein metabolism. I. Urinary creatinine after castration. I. SCHRIRE and H. ZWARENSTEIN (Biochem. J., 1932, 26, 118—121).—Castration causes a 25—50% increase in the urinary creatinine of adult male rabbits. The normal excretion is re-established in a few weeks by a graft of testes. Removal of the graft again increases creatinine excretion.
A. COHEN.

Exact evaluation of the specific hormone of the corpus luteum. C. CLAUBERG (Klin. Woch., 1931, 10, 1949—1952; Chem. Zentr., 1931, ii, 3222).—If much follicular hormone is present together with the luteohormone there is an increase in the growth of the uterine muscle. Limiting vals. are given.
A. A. ELDRIDGE.

Function of the endocrine glands on the sugar-excretion threshold. S. YOKOTA (J. Biochem. Japan, 1932, 15, 65—110).—The sugar threshold val., which in the rabbit is normally 0.17—0.20%, is lowered by, transplantation of suprarenal cortex whilst the assimilation is increased. Destruction of the cortical substance is generally accompanied by a rise in the leak-point, whilst the assimilation is unchanged. The leak-point is also increased in adrenaline glycosuria and lowered by destruction of the adrenal medulla. Orally administered thyroid gland or injected thyroxine induces an increase in the threshold val. and a decrease in the assimilation, whilst thyroidectomy has the opposite effect. Injection of pituitrin results in a temporary decrease followed by an increase in the threshold val. and in the sugar tolerance whilst the assimilation is significantly decreased. Subcutaneous administration of anterior pituitary lobe extracts produces a significant fall both in threshold val. and sugar tolerance frequently accompanied by an increase in the assimilation; unlike pituitrin, no increase in the fasting blood-sugar is effected.
F. O. HOWITT.

Influence of cryptorchidism on the gaseous and nitrogenous metabolism of rats. V. KORENCHESKY and M. DENNISON (Biochem. J., 1932, 26, 429—434).—The max. increase of gaseous metabolism occurs during the period of greatest resorption of the seminiferous cells. After this period the wt. of the animals returns towards or reaches normal and even in some cases increases. There is a deposition of N in the body, in some rats remaining at or exceeding the normal level even during the period of increased gaseous metabolism.
S. S. ZILVA.

Hormone-like diuresis-promoting and -inhibiting substances in human and animal urine.

J. OLIVET (Z. ges. exp. Med., 1931, 78, 650—694; Chem. Zentr., 1931, ii, 2630).—Serum of rabbits suffering diuresis owing to injury of the vermiform process, when injected into other animals, causes polyuria. Extracts having a diuretic action can be obtained from the urine of man and animals.
A. A. ELDRIDGE.

Lovibond value of liver oils of animals and promotion of growth by vitamin preparations P. KARRER, H. VON EULER, and K. SCHÖPP (Helv. Chim. Acta, 1932, 15, 493—495).—The Carr-Price reaction for vitamin-A is applied to the liver oils from a variety of animals, and numerous vitamin-A preps. from such are tested biologically.
H. A. PIGGOTT.

Calcium-phosphorus metabolism in the chicken. III. Influence of cereals and vitamins-A and -D. E. J. KING and G. E. HALL (Poultry Sci., 1931, 10, 332—352).—The anticacifying action of oatmeal was increased by boiling the meal with 1% HCl followed by neutralisation with NaOH. Data concerning the ash, Ca, P, and phosphatase content of the bones and the Ca and P content of the blood-serum are tabulated.
CHEMICAL ABSTRACTS.

Halibut-liver oil as a source of vitamin-A. J. A. LOVERN (Nature, 1932, 129, 726).—The vitamin-A content of halibut-liver oil varies irregularly from 30 to 1600 blue units in 0.2 c.c. of 20% solution.
L. S. THEOBALD.

Photochemistry of vitamins-A, -B, -C, and -D. F. P. BOWDEN and C. P. SNOW (Nature, 1932, 129, 720—721).—The absorption spectrum of β -carotene contains an additional weak band at 2700 Å. A solution of carotene in cyclohexane, irradiated in an atm. of N_2 by the Hg line 2650 Å., shows the band at 3280 Å. associated with vitamin-A. The solution gives a blue colour with SbCl_3 in CHCl_3 . Vitamin-A is destroyed by light of wave-length 3130 Å. which eliminates the 3280 Å. band in a few hr. Vitamin- B_1 shows 3 bands at 2600, 2400, and 2100 Å. Irradiation by the Hg line 2537 Å. reduces the intensity of the 2600 Å. band and destroys the B_1 activity towards rats. Vitamin- B_1 deactivated by heating with alkali shows a similar absorption spectrum with the 2600 Å. band again missing. Hexuronic acid gives at 2650 Å. a strong band which is practically unaffected by irradiation. Light of wave-length 3000 and 2850 Å. has no effect on the absorption spectrum of narcotine, but a wave-length of 2400 Å. produces a complete change in the spectrum which, after irradiation, consists of a single band at 2900 Å. The 2967 Å. Hg line produces a strong absorption in the calciferol region when used to irradiate ergosterol. Calciferol is completely destroyed by irradiation for 1 hr. with the Hg lines 2650 or 2537 Å.; a slow destruction occurs with the line 3130 Å.
L. S. THEOBALD.

Interpretation of the colour match in the anti-mony trichloride test for vitamin-A. R. S. MORGAN (Biochem. J., 1932, 26, 377—380).—The blue reading in the Lovibond match of CuSO_4 solution varies widely as the quality of the light from the solution is varied by interposition of red glasses. The variation obtained is similar to that given in the colour matches on a wide range of oils and concen-

trates. The "blue minus yellow" val., however, remains const. and is independent of the interposition of red. This val. is therefore recommended as a criterion for vitamin-A. S. S. ZILVA.

Absorption and elimination of lipins during vitamin-A deficiency. L. EMERIQUE (Bull. Soc. Chim. biol., 1932, 14, 305—312).—Ingestion of different amounts of fat by rats fed on diets lacking in vitamin-A has no effect on the time required for the symptoms of the deficiency to appear. The utilisation of factor-A is not influenced by the fat content of the diet, and there is no decrease with time in the absorption of fat from the diet during the deficiency.

A. LAWSON.

Pecan nut as source of vitamin-A. H. LEVINE (J. Home Econ., 1932, 24, 49—53).—The nut contains about 3—6 (Sherman and Smith) units per g.

CHEMICAL ABSTRACTS.

Absorption spectrum of vitamin-A concentrates. J. W. WOODROW and J. B. PHILIPSON (Proc. Iowa Acad. Sci., 1930, 37, 310).—Prominent bands occur at 310 and 328 μ , and minor bands at 323 and 340 μ .

CHEMICAL ABSTRACTS.

Vitamin-A and carotene. IX. Conversion of carotene into vitamin-A in the cow. T. MOORE (Biochem. J., 1932, 26, 1—9).—Small quantities of carotene are found in the body-fat of cows but vitamin-A accumulates in the liver- and milk-fats. In spite of the large amount of carotene available during pasture feeding, the output of carotene and vitamin-A is restricted by liver-storage of reserves which are depleted during stall-feeding. At the end of winter, addition of carotene to the diet increases the carotene and vitamin-A content of the butter-fat. Carotene therefore appears to be converted into vitamin-A as in the rat (A., 1930, 962). Jersey cows yield a butter-fat more highly pigmented than that of shorthorns.

A. COHEN.

Sparing action of fat on vitamin-B. II. Rôle played by m. p. and degree of unsaturation of various fats. III. Rôle of glycerides of single fatty acids. H. M. EVANS and S. LEPKOVSKY (J. Biol. Chem., 1932, 96, 165—177; cf. A., 1929, 852, 1203).—II. The effect of fats in diminishing the dose of vitamin-B necessary for a definite growth performance is independent of their degree of saturation and of their m. p., provided it is low enough for absorption. The effect is unchanged by hydrogenation at 170°, or under pressure, by saponification, distillation, or esterification with glycerol at 230°.

III. In presence of vitamin-B, natural fat is superior in effect on growth to any single glyceride; in absence of vitamin-B some pure glycerides are better, especially myristin and caprylin. The most favourable fatty acids do not necessarily resemble each other in m. p. or length of chain.

J. B. BATEMAN.

Rôle of the vitamin-B complex and alimentary balance in the utilisation of protein. R. LECOQ (Compt. rend., 1932, 194, 1267—1269).—Pigeons fed on various diets deficient in vitamins-B never fail to develop symptoms of avitaminosis even when the diet is rich in protein and poor in carbohydrate,

but under the latter condition the development of symptoms tends to be delayed. With diet lacking vitamins-B and containing various proportions of fat, carbohydrates, and proteins, the addition of brewer's yeast is always beneficial, but even in the presence of vitamins-B the best results are obtained when the constituents of the diet are present in proportion similar to that existing in cow's milk.

W. O. KERMAK.

Isolation of crystalline oryzanin. I. S. OTAKE (J. Agric. Chem. Soc. Japan, 1931, 7, 775—808).—Active (antineuritic) oryzanin (33 g.), obtained from rice bran (100 kg.), was dissolved in H₂O and H₂SO₄ added to p_H 2.6; AgNO₃ was added, and adenine and hypoxanthine were isolated from the ppt. The filtrate was treated with Ba(OH)₂ to p_H 2.5—4.5; nicotinic acid and adenine were isolated from the ppt. The ppt. obtained on further addition of Ba(OH)₂ to p_H 4.5—6.8 afforded nicotinic acid, a base, C₃H₆N₂ (hydrochloride, m. p. 262°), and oryzanin hydrochloride, C₆H₈O₂N₂.HCl, m. p. 250°, resembling Jansen's cryst. vitamin-B. The AgNO₃-Ba(OH)₂ ppt. at p_H 6.8—9.0 afforded nicotinic acid; the filtrate on treatment with phosphotungstic acid yielded choline and a base, C₈H₁₀O₃N (hydrochloride, m. p. 204—205°).

CHEMICAL ABSTRACTS.

Antineuritic vitamin. II. Removal of impurities by oxidising agents. R. J. BLOCK and G. R. COWGILL (J. Biol. Chem., 1932, 96, 127—132).—The action of various oxidising agents on vitamin-B₁ concentrates was investigated. Modification of the CCl₄ process for the purification of the vitamin (this vol., 309) to include the use of H₂O₂ for oxidation of carbohydrate impurities results in a considerable purification without loss of the antineuritic factor.

F. O. HOWITT.

Vitamin-C in goat's and cow's milk. J. C. DE R. DE WILDT and E. BROUWER (Vereen. Expl. Proofzuiv. Hoorn, 1930, 11—20; Chem. Zentr., 1932, i, 412).—The vitamin-C content is the same for both milks; also the vals. for summer and winter milk are very closely similar.

A. A. ELDRIDGE.

Chemical nature of vitamin-C. C. G. KING and W. A. WAUGH (Science, 1932, 75, 357—358).—Vitamin-C, conc. from lemon juice and recryst. from org. solvents, corresponds with a hexuronic acid (cf. this vol., 548). In daily doses of 0.5 mg. it protects growing guinea-pigs from scurvy and permits normal vitality in animals fed on a vitamin-C-free diet.

L. S. THEOBALD.

Hexuronic acid as the antiscorbutic factor. J. L. SVIRBELY and A. SZENT-GYÖRGYI (Nature, 1932, 129, 690).—The animals treated with hexuronic acid (cf. this vol., 548) showed no scurvy after 90 days. Vitamin-C is therefore concluded to be a single substance identical with hexuronic acid. Other claims (see above) appear to need the support of a chemical analysis and a specification of the test period.

L. S. THEOBALD.

Hexuronic acid as the antiscorbutic factor. S. S. ZILVA (Nature, 1932, 129, 690).—Critical (cf. preceding abstract). Hexuronic acid and the antiscorbutic factor may not be identical.

L. S. THEOBALD.

Reduction capacity of plant foodstuffs and its relation to vitamin-*C*. III. Quantities of reducing substance in various fruits and vegetables. J. TILLMANS, P. HIRSCH, and J. JACKISCH. IV. Reversibility of the oxidation of the reducing substances in lemon-juice. J. TILLMANS, P. HIRSCH, and H. DICK. V. Antiscorbutic action of various extracts of cucumber. J. TILLMANS, P. HIRSCH, and J. JACKISCH (*Z. Unters. Lebensm.*, 1932, 63, 241—267, 267—275, 276—283).—III. The authors' method (this vol., 310) gives results parallel with animal experiments if the samples are extracted with a 4-fold vol. of 3% H_2SO_4 for 4 min., H_2O or cold acid giving lower results; coloured liquids are first extracted with $PhNO_2$. Exceptions (*e.g.*, preserves) were due to the presence of metallic salts. Titration with $Na_2S_2O_3$ of the excess of 0.001*N*-I unabsorbed after 1 min. is less sp., and often gives high results, particularly for old solutions. The ratios, max. no. of c.c. of 0.001*N*-indicator equiv. to 100 g. of sample/Hahn's guinea-pig unit, are calc., and the 130 samples are classified. The high vals. from leaf vegetables cannot be attributed to reducing substances other than those associated with vitamin-*C*.

IV. The reducing substances associated with vitamin-*C* (see above, also this vol., 310) may be oxidised by 2:6-dichlorophenol-indophenol by atm. O_2 or H_2O_2 in the warm, or by Cl or I. This oxidation may be reversed (except for O_2 and only partly for Cl) by the action of H_2S for 24 hr., excess being then removed in N_2 ; Pd- H_2 is without effect. The reversal is less rapid at low temp., and is incomplete if the juice is not fresh or if the H_2S is not added soon after the oxidising agent.

V. Animal experiments with hot and cold extracts of cucumber indicate that for aq. extracts the reducing substance associated with vitamin-*C* activity (see above) is more easily oxidised by atm. O_2 than that obtained from lemon-juice. It is also concluded that the oxidation product is not present originally in the cucumber. The titration val. of a H_2SO_4 extract is not raised by the action of H_2S for 1 hr. followed by removal of the excess in a vac., but that of 5 c.c. of juice from a ripe cucumber fell from 2.2 to 0.25 c.c. after 24 hr. in CO_2 , but was raised to 3.9 c.c. by subsequent treatment with H_2S .

J. GRANT.

Properties and structures of crystalline vitamins. J. D. BERNAL (*Nature*, 1932, 129, 721).—The changes produced in solutions of ergosterol and calciferol by irradiation in monochromatic ultraviolet light can be produced in the crystals and can be observed by the progressive alteration from anisotropic to isotropic material. Ergosterol is changed, presumably to calciferol, by light of 2967 Å., but scarcely at all in 3650, 3130, and 2537 Å. Calciferol is stable at 3650 and 2537 Å. but is destroyed at 3130 Å. Ring mols. are indicated for the structures of vitamin-*B* and hexuronic acid, whilst crystals of β -carotene and α -crocin do not show the long spacings expected from their constitution.

L. S. THEOBALD.

Crystalline vitamin-*D*. C. E. BILLS and F. G. MACDONALD (*J. Biol. Chem.*, 1932, 96, 189—194).—Impure resins, potency 25,000 units per mg., stored

at 0° in CO_2 , crystallised slowly after several weeks. Irradiated ergosterol preps. have marked tendency to form mixed crystals, suggesting that all the cryst. products hitherto described are isomorphous mixtures, containing much inert material. These products show wide variation in antirachitic val.

J. B. BATEMAN.

Vitamin-*D* deficiency and anæmia. H. HAUSS (*Z. Vitaminforsch.*, 1932, 1, 26—38).—Anæmia in rickets is not due to vitamin-*D* deficiency.

H. DAVSON.

Action of vitamin preparations on bactericidal powers of blood. T. HØLSEN (*Z. Vitaminforsch.*, 1932, 1, 3—25).—A daily dose of 60 c.c. of a 1% "vigantol" solution increases the resistance of the rabbit's blood to *Staphylococci*; hypervitaminosis decreases this resistance, an effect which may be counteracted by simultaneous administration of yeast. The latter seems to neutralise the poisonous action of "vigantol." "Pro Ossa," containing vitamins-*A* and -*D*, increases the resistance to *Staphylococci*.

H. DAVSON.

Photographic records of vitamin-*D* line tests. H. STEVENS and E. M. NELSON (*Ind. Eng. Chem. [Anal.]*, 1932, 4, 200—201).—A staining procedure and a photomicrographic apparatus are described.

E. S. HEDGES.

Mode of action of irradiated ergosterol. I. Effect on the calcium, phosphorus, and nitrogen metabolism of normal individuals. W. BAUER, A. MARBLE, and D. CLAFLIN. II. Effect on the calcium and phosphorus metabolism of individuals with calcium-deficiency diseases. III. Effect on formation of bone trabeculæ. W. BAUER and A. MARBLE. IV. Hyperparathyroidism. W. BAUER, A. MARBLE, and D. CLAFLIN (*J. Clin. Invest.*, 1932, 11, 1—19, 21—35, 37—45, 47—62).—I. Small doses produced no const. change in Ca or P metabolism; 30 mg. per day caused an increase in faecal and a decrease in urinary Ca and P, the quantities being reversed later. The Ca and P balances and the serum-Ca, -P, and -N were only slightly affected.

II. When there is a deficiency of Ca in the serum or bones, ergosterol therapy produces Ca retention.

IV. The beneficial results are directly related to the Ca intake. On a high Ca intake, with ergosterol, there were: decreased faecal Ca, increased urinary Ca, positive Ca balance, serum-Ca, faecal and urinary P; a fall in positive P balance and serum-P; and a rise in the product of serum-Ca and -P.

CHEMICAL ABSTRACTS.

Photochemistry of ergosterol. E. H. REERINK and A. VAN WIJK.—See this vol., 480.

Hormones and ergosterol intoxication. M. HAENDEL and J. MALET (*Rev. asoc. méd. Argentina*, 1929, 42, 295—324).—The toxic effects on rabbits of large doses of irradiated ergosterol are diminished by concurrent administration of insulin or sexual hormone, and increased by that of adrenaline, thyroïdin, or hypophysin.

CHEMICAL ABSTRACTS.

Vitamin-*D* content of red palm oil. W. J. DANN (*Biochem. J.*, 1932, 26, 151—154).—Four samples of red palm oil showed very little antirachitic

activity, 100 mg. daily of the richest (native) oil being insufficient to protect rats from rickets. The oil is recommended as a source of vitamin-A free from vitamin-D.

A. COHEN.

Determination of vitamin-D. K. M. KEY and B. G. E. MORGAN (Biochem. J., 1932, 26, 196—207).—The curative effect on rats of graded doses of vitamin-D has been determined by reference to Dyer's scale of healing (cf. this vol., 97). Curves relating degree of healing to dosage are similar to those of Dyer, give similar results for the vitamin-D val. of unknown substances, and agree with results of prophylactic tests in which ash content of fat-free bone is determined. A change in the Ca : P ratio in Steenbock's rachitogenic diet from 4 : 1 to 2 : 1 is equiv. to the antirachitic effect of a daily dose of 0.7 unit of vitamin-D.

A. COHEN.

Determination of vitamin-D. I. Relationship between graded doses of a standard solution of vitamin-D, administered to young rats on a rachitogenic diet, and the ash content of their bones. E. M. HUME, M. PICKERSGILL, and M. M. GAFFIKIN (Biochem. J., 1932, 26, 488—505).—With groups of animals of the same litter composition on different doses with 10—20 animals per dose, smooth curves are obtained. When the vals. for the percentage ash are plotted against the logarithms of the doses (with the exception of the lowest and the highest) a linear relationship between the two variables is revealed. For assaying purposes two groups of 8—10 young rats receive suitable doses of irradiated ergosterol, whilst two other groups of animals similarly constituted as regards litter and sex receive two doses of the unknown substance. The average result of the groups receiving the unknown dose is then read from curves which have been constructed to correlate doses of a standard solution of irradiated ergosterol administered prophylactically with the percentage of ash in the bones of young rats on a rachitogenic diet. If the resulting vals. for the doses of the standard do not fall directly on one of the curves, the experiment is repeated. If they do not fall on any of the curves, a graph in which the ash vals. are plotted against logarithms of the doses is employed, since these graphs are straight lines, and a knowledge of two points is sufficient to construct the whole graph.

S. S. ZILVA.

Determination of vitamin-D. II. Comparison of radiography and bone analysis in the estimation of vitamin-D. III. Stability of preparations of vitamin-D. R. B. BOURDELLON, H. M. BRUCE, and T. A. WEBSTER (Biochem. J., 1932, 26, 506—521, 522—530).—II. A radiographic scale is described showing various degrees of development of rickets for use in determination of vitamin-D by measurement of its prophylactic effect. The error in the determination of the resultant effect is considerably greater with the radiographic scale than with bone analysis. The chief variations in the sensitivity of a stock of rats fed on a supposedly const. diet are probably due to some factor other than vitamin-D. The prophylactic radiographic scale is less satisfactory than the curative scale.

III. Vitamin-D in solution in olive oil may de-

teriorate seriously if kept at room temp. for periods of a year or more. Deterioration at 0° has not been detected in the time available. Extrapolation from results at higher temp. suggests that preps. at 0° may lose half their activity in about 3 years, but there is some reason to think that the solidification of the oil has a preservative effect and that the stability at 0° may be greater than the experiments suggest. The addition of various common substances likely to be present as impurities has no very great effect with the exception of S which causes deterioration.

S. S. ZILVA.

Apparatus for determination of carbon dioxide and oxygen of respiration [of fruit]. M. H. HALLER and D. H. ROSE (Science, 1932, 75, 439—440).

L. S. THEOBALD.

Biological effect of associated water molecules. H. T. BARNES and T. C. BARNES (Nature, 1932, 129, 691).—H₂O from recently condensed steam, containing less trihydrol, causes filaments of *Spirogyra* to assume a colourless mass occupying less vol. than the filaments in trihydrol H₂O which maintains the rigidity and turgor of the cells.

L. S. THEOBALD.

Biological degradation of chlorophyll. II. Phyllobombycin and probophorbide. H. FISCHER and A. HENDSCHEL (Z. physiol. Chem., 1932, 206, 255—273; cf. A., 1931, 966).—Hydrolysis of phyllobombycin with KOH in MeOH or PrOH gives a mixture of uncrystallisable chlorins, including chlorin *e*. Treatment with HBr in AcOH at 170° or with HCO₂H at 140° gives small amounts of deoxyphylloerythrin and rhodoporphyrin ester. With HBr-AcOH at 50° phylloerythrin was produced and identified spectroscopically. Reduction with HI after treatment with O₂ led to the isolation of phæoporphyrin *a*₅ ester. Phyllobombycin, treated with diazomethane without crystallisation, gave the cryst. Me₃ ester (I), m. p. 264° (Fe, Zn, and Cu salts), identical with phæopurpurin 18 Me₃ ester. Reduction of (I) with HI in AcOH gave an ester, m. p. 224°, spectroscopically resembling chloroporphyrin *e*₄ ester. HBr and AcOH at 170° produced isophæoporphyrin *a*₄. At 50°, traces of phylloerythrin together with chloroporphyrin *e*₆ were obtained. When treated with pyridine and Na₂CO₃, (I) gave pseudoverdoporphyrin. Phyllobombycin must contain a nucleus with a propionic acid, a nuclear CO₂H, and an OAc radical (the two last from the reductive hydrolytic fission of the isocyclic ring of chlorophyll).

Phylloerythrin was obtained from sheep faeces. Coproporphyrin was also detected and four probophorbides were isolated as the esters: *a* (Me ester, m. p. 226°; oxime; Fe salt); *b* (Me ester, m. p. 207°); *c* (Me ester, m. p. 233°); *d* (Me ester, m. p. 230°). These probophorbides are divided spectroscopically into two groups: (i) *a*, *c*, *d* and (ii) *b*. The analysis of *b* gives the constitution C₃₆H₄₀O₆N₄; with HI *b* yields chloroporphyrin *e*₆ and traces of phylloerythrin. It is closely related to phyllobombycin. Probophorbide *a* resembles phylloerythrin and is converted into the latter by HI in AcOH. Probophorbides *c* and *d* contain more H and OMe than *a* but are easily converted into phylloerythrin.

Winter faeces of rabbits contained phylloerythrin

and a chlorin, isolated as the *Me* ester (diazomethane), m. p. 221°. The crude Et₂O extract after 3 min. with HI in AcOH at 65° gave rhodoporphyrin. Treatment of phaeophytin with HI in AcOH for 2 min. gave phaeoporphyrin α_5 , which when heated for 24 hr. with HBr in AcOH at 50—55° gave phylloerythrin.

J. H. BIRKINSHAW.

Formation of chlorophyll in roots exposed to light, especially in the roots of barley. R. J. GAUTHERET (Compt. rend., 1932, 194, 1510—1513).—The roots of barley may develop a green colour due to chlorophyll when placed in light, the most marked results being obtained with isolated roots detached from the plant. Glucose or fructose added to the medium has a favourable effect.

W. O. KERMACK.

Absorption and migration of nitrogen in the leaves of *Salix fragilis*, L. N. T. DELEANO and M. ANDRESCO (Bul. Soc. Stiinte Cluj, 1931, 6, 209—220; Chem. Zentr., 1932, i, 537).—Three stages in the life cycle are: growth (25%), assimilation period (50%), N-migration (25%). In the last period the N is present chiefly as NH₃ and NH₂-acids; the quantity of albumin-N falls.

A. A. ELDRIDGE.

Stimulation of growth and metabolism in wheat tissue. A. RADOEFF (Compt. rend., 1932, 194, 1527—1529).—The stimulation of the growth of wheat embryos which is produced by Mg and Mn and to only a very slight extent by Zn, Fe, and Cu, is not accompanied by any significant increase in the metabolic rate measured by the O₂ and CO₂ exchange.

W. O. KERMACK.

Wax metabolism in the leaves of Brussels sprout. P. N. SAHAI and A. C. CHIBNALL (Biochem. J., 1931, 26, 403—412).—The following constituents were identified in the leaf-wax: *n*-nonacosane, 15-nonacosanone, 15-nonacosanol, ceryl alcohol, cerotic acid, and probably *n*-hentriacontane. Olefines were absent. The seeds contain no wax, but synthesis takes place rapidly in all parts of the embryo and proceeds continuously in the leaf throughout the life-history of the plant. The composition of the wax does not alter throughout this period and there is no evidence that the paraffin is formed by reduction of the ketone. All the components of the wax are probably end-products of metabolism.

S. S. ZILVA.

Synthesis and metabolism in cultivated plants. S. ODÉN and K. SJÖBERG (Medd. Centr. Försöksvas. Jordbruk., 1931, No. 386, 3—56; Chem. Zentr., 1931, ii, 3109).—The increase in N and mineral constituents is most marked during the first half of the vegetative period. The carbohydrate content undergoes large variations.

A. A. ELDRIDGE.

Utilisation of excess mineral matter in the leaf in relation to growth of the plant. H. LEGATU and L. MAUME (Compt. rend., 1932, 194, 933—935).—An increased K content of the leaves of the potato is no criterion of the wt. of fresh tubers obtained.

P. G. MARSHALL.

Rôle of plastids and of the cytoplasm in amylogenic condensation. A. MAIGE (Compt. rend., 1932, 194, 1376—1378).—A discussion of the formation of starch in plant cells. The plastids are prob-

ably concerned with the conversion of the proenzyme into the active amylogenese which effects condensation.

W. O. KERMACK.

Absorption of salts by plant tissues. G. E. BRIGGS (Ann. Bot., 1932, 46, 301—322).—Recent work is discussed and evidence advanced to show that the mechanism of salt intake by plants from dil. solutions is by an exchange of anions between solution and cell-sap and of cations between solution and cytoplasm. From more conc. solutions of single salts both anions and cations pass into the sap. In very dil. solutions leaching of ions from cytoplasm and sap is significant.

A. G. POLLARD.

Plant nutrition. III. Effect of potash deficiency on the rate and respiration in leaves of barley. F. J. RICHARDS (Ann. Bot., 1932, 46, 367—388).—Differences in the ratio of dry wt. to leaf area in barley plants grown with varying proportions of K are almost entirely attributable to differences in H₂O content. Leaf-to-leaf variations in the same plant result from differences in anatomical structure. With decreasing proportions of K in the nutrient, respiration rates increase up to a max., subsequently falling with further dilution of the nutrient. These facts are discussed in relation to the carbohydrate and NH₂-acid content of the leaves. The K content of leaves varies with that of the nutrient, but the relationship is not linear. From leaves rich in K leaching of the element by rain is probable, but no leaching occurs from K-deficient plants.

A. G. POLLARD.

Reserve polysaccharide of the seeds of fennugreek. Digestibility and fate during germination. K. M. DAOUD (Biochem. J., 1932, 26, 255—263).—Acid hydrolysis of the polysaccharide yields equiv. amounts of mannose and galactose. The polysaccharide, which is a salt of a silicophosphoric ester of mannogalactan, is not hydrolysed by saliva or pancreatic extract, and does not alter the blood-sugar after ingestion. During germination of the seeds the mannose and galactose are converted into glucose, fructose, and sucrose.

A. COHEN.

Determination of glutamine in presence of asparagine. A. C. CHIBNALL and R. G. WESTALL (Biochem. J., 1932, 26, 122—132).—In the reaction with HNO₂ in the Van Slyke determination 92% of the total N of glutamine appears as NH₂-N. After heating glutamine 3 hr. at 100° at *p*_H 8, the amide-N and NH₂-N are 35.5% and 8.5% of the total N, respectively. Asparagine is stable and gives normal vals. The results are employed to determine the glutamine and asparagine contents of mixtures of these substances and of plant extracts, several cases of which are quoted.

A. COHEN.

Relations between the physiological and geological characters of a forest of *Cryptomeria japonica* and soil conditions. K. MORIKAWA (Bull. Coll. Agric. Kyushu Fukuoka, 1931, 4, No. 4; Proc. Internat. Soc. Soil Sci., 1932, 7, 31).—Transpiration rates and the H₂O and ash contents of leaves varied in parallel with growth rates.

A. G. POLLARD.

Fat, lecithin, and protein of the soya bean. H. KÜHL (Pharm. Zentr., 1932, 73, 243—248).—A review.

Separation of growth-promoting substances. N. NIELSEN and V. HARTELUS (Compt. rend. Lab. Carlsberg, 1932, 19, No. 8, 17 pp.; cf. A., 1931, 1091, 1334).—*Rhizopus sinuis* forms two growth-promoting substances when grown in a NH_4 tartrate-glucose medium. One, substance A, is sol. in Et_2O , is readily destroyed on oxidation by H_2O_2 , and promotes the growth of *Avena* coleoptiles as shown by the bending reaction. The other, substance B, is insol. in Et_2O , is not oxidised by H_2O_2 , and promotes the growth of *Aspergillus niger*. Both substances are stable to heat.

F. O. HOWITT.

Chemistry of the plant growth-promoting substance. F. KÖGL and R. J. HAAGEN-SMIT (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1411—1416).—A unit is defined as the least quantity of active substance which, under standard conditions, will cause a bending of 10° in the decapitate coleoptile of *Avena sativa* within 2 hr. The activity of products from various sources is given. The active principle is obtained as a by-product in the prep. of oestrin from pregnancy urine. A NaHCO_3 extract of the urine is acidified and extracted with Et_2O . Inactive impurity is removed by boiling light petroleum, the insol. residue having an activity of 130,000 units per mg. It is dissolved in aq. EtOH and the solution extracted with C_6H_6 , the hormone remaining in the former. Further purification *via* the Pb salt yields a product of 10^6 units per mg. The active principle after distillation at $125\text{--}130^\circ/0.1$ mm. has an activity of 5×10^6 units per mg. Two crystallisations from aq. COMe_2 yield a product, m. p. 172° (uncorr.) (C 68.62, H 10.18%), with an activity of 30×10^6 units per mg. The name *auxin* is suggested. Theelin (Parke Davis, 50 R.U. per c.c.) is inactive as regards growth effect in contrast to some preps. of progynon.

P. G. MARSHALL.

Flow of sap in plants. B. HUBER (Ber. deut. bot. Ges., 1932, 50, 89—109).—The rate of flow of sap is determined by the rate of transmission of heat from a locally warmed stem area to a thermocouple. Radioactive substances (*e.g.*, Th-B) are successful indicators of sap flow.

A. G. POLLARD.

Relations between the growth of various parts of the melon seedling and the quantity of reserves left for the embryo. P. CHOUARD and G. TEISSIER (Compt. rend., 1932, 194, 1513—1515).—Removal of part of the food reserves from the seeds of *Cucumis melo* results in a general decrease in size of the resulting embryo, but the relative size of the parts is not significantly altered.

W. O. KERMACK.

Stomatal movement and hydrogen-ion concentration. E. P. SMITH and M. S. JOLLY (Nature, 1932, 129, 544).—The p_{H} vals. at which the stomata of the guard-cells of *Tulipa*, *Scilla*, *Iris*, and *Tradescantia* are open in solutions of CO_2 , and in B.D.H. "universal buffer mixture," are recorded.

L. S. THEOBALD.

Radioactivity and the germination of bulbs. D. MONTET (Compt. rend., 1932, 194, 1093—1095).—With the hyacinth and tulip a more fully developed foliage is obtained under the influence of radioactivity, whether supplied in the form of Ra emanation

or U_2O_5 . The optimum quantity of the latter for increased growth of the tulip is 0.5 g. per 1500 g. of soil.

P. G. MARSHALL.

Action of Italian radioactive soils on germination of seeds and on growth of plants. G. MEZZADROLI and E. VARETON (Atti R. Accad. Lincei, 1931, [vi], 14, 443—447).—With plants grown in Knopp's nutrient solution, addition of finely ground radioactive soil showing 4.2×10^{-9} g. of Ra per g. causes marked increases in the root and plant growth. In field experiments, the use of the soil as fertiliser results in greener and stronger plants and in increase of the crop by at least 20%.

T. H. POPE.

Direct versus indirect effects on potato-amylase by chemicals which induce sprouting of dormant tubers. F. E. DENNY (Contr. Boyce Thompson Inst., 1932, 4, 53—63).—The effect of certain chemicals (*e.g.*, ethylene chlorohydrin, NaCNS, and KCNS) on the amylase activity of expressed potato juice (direct effect) was not related to their action in stimulating the sprouting of the tubers, nor to changes in amylase activity produced subsequent to treatment of the whole tissue with these substances (indirect effect). Sprouting response was more nearly related to the indirect amylase effect. KNO_3 and KCl were not markedly active in inducing sprouting and had little effect on amylase activity. The sprouting response to chemical treatment is indirect and is not dependent on the development of high amylase activity in treated tubers.

A. G. POLLARD.

Development and ripening of peaches as correlated with physical characteristics, chemical composition, and histological structure of the fruit flesh. I. Physical measurements of growth and flesh texture in relation to the market and edible qualities of the fruit. M. A. BLAKE, O. W. DAVIDSON, R. M. ADDOMS, and G. T. NIGHTINGALE (New Jersey Agric. Exp. Sta. Bull., 1931, No. 525, 35 pp.; cf. A., 1931, 273).—The increased vegetative activity and production of tender growth resulting from high N feeding occurs independently of the nature of the N source. Repeated treatment with N fertilisers or certain systems of cultural operations produce a high N-low carbohydrate type of tree. Treatments of an opposite character produce a low N-high carbohydrate type.

A. G. POLLARD.

Origin of the uronic acids in the humus of soil, peat, and composts. S. A. WAKSMAN and H. W. REUSZER (Soil Sci., 1932, 33, 135—151).—During the biological decomp. of plant residues, true pentosans are attacked more readily than uronic acid complexes. In different plant materials the relative proportions of various hemicelluloses and the relative ease of decomp. varies considerably. Manuring of soil causes an increase in pentosan content. Prolonged cultivation without the addition of org. matter results in a decreased humus content and a relative increase in uronic acids.

A. G. POLLARD.

Apparatus for continuous extraction of plant materials with ether under tropical conditions. W. J. BLACKIE (J.S.C.I., 1932, 51, 129—130r).—The apparatus is designed to extract 100 g. of material.

Vapour and siphon tubes are carried by a glass connecting piece which is attached at each end by long ground-glass joints to boiling flask (1500 c.c.) and extractor (7×30 cm.). The latter is connected by a ground-glass joint with Hg seal to a worm condenser.

C. W. DAVIES.

Lignin-like complexes in fungi. C. THOM and M. PHILLIPS (J. Wash. Acad. Sci., 1932, 22, 237—239).—Brown-walled moulds such as *Cladosporium* and *Alternaria* contain 17—29% of lignin-like substances, and brown-walled bracket fungi such as *Trametes pini* and *Fomes igniarius* larger proportions. Light-coloured bracket fungi contain very little.

C. W. GIBBY.

Composition of the cell membrane of the alder (*Alnus glutinosa*). K. NEVROS (Praktika, 1931, 6, 270—274; Chem. Zentr., 1932, i, 536).—Schmidt's improved ClO_2 method was employed in the determination of the cellulose:xylan ratio. 0.01—0.2% NaOH removed the carboxyl substances consisting of 2 acids and xylan; with >0.2% the pentosan begins to dissolve, and with 9% max. solubility occurs, with dissolution of cellulose constituents. Attack by 5—7% NaOH on the cellulose is diminished by addition of 3% NaCl without diminution of the solubility of the skeletal substance. The acid-free substance remaining after treatment of the latter with 0.05N-NaOH contains $3\text{C}_6\text{H}_{10}\text{O}_5 : 1\text{C}_5\text{H}_8\text{O}_4$. Hence the cellulose and the H_2O -sol. xylan are chemically combined.

A. A. ELDRIDGE.

Juice of the Maguey plant (*Manso fino*). I. H. D. JONES (J. Amer. Pharm. Assoc., 1932, 21, 354—356).—The composition, properties, and reactions of "aguamiel," the fresh juice of *Agave atrovirens*, Karw, and of the syrup are given.

E. H. SHARPLES.

New vegetable constituent: uric acid. R. FOSSE, P. DE GRAEVE, and P. E. THOMAS (Compt. rend., 1932, 194, 1408—1413).—Uric acid exists in many plants and especially in grains, and has been isolated in a pure form from the seeds of *Melilotus officinalis*.

W. O. KERMAK.

Non-alkaloidal fraction of ergot. H. LANG-ECKER (Arch. exp. Path. Pharm., 1932, 165, 299—324).—The separation of the alkaloids from the amines in extracts of ergot and the standardisation of the latter by comparison with histamine in their action on the small intestine and uterus of the guinea-pig were investigated. The "intestine val." is less than the "uterus val.," but with increasing purity the vals. tend to agree, indicating that the intestine method is sp. for the amine fraction. In ergot preps. the average amine content is lower than the alkaloid content, but the former exhibits a greater stability. Ergotamine (1:40,000) suppresses the tonus action of histamine in the surviving guinea-pig intestine. CO_2 , H_2S , or increased acidity greatly diminishes this action to an extent which is not influenced by the age of the extract. Bacterial infection of the extracts occasionally leads to increased action on the intestine and uterus. Thus following bacterial fermentation a material can be separated which closely resembles, but is not identical with, histamine, although traces of the latter are present.

F. O. HOWITT.

Glucoside fractions of *Digitalis* leaves. M. GUGGENHEIM, K. FROMHERZ, and W. KARRER (Arch. exp. Path. Pharm., 1932, 165, 412—415).—The work of Hockstra (A., 1931, 1453) is criticised on the grounds that the fractions of *Digitalis* glucosides prepared, e.g., digitoxin, gitalin, and bigitalin, neither were identical with the pure glucosides nor even represented specimens in which the respective glucoside predominated. Hence the quant. fractionation method employed is erroneous. Also digalen occurs in *D. purpurea* and not in *D. lutea*.

F. O. HOWITT.

New glucoside, citronin, from peel of *Citrus limon*. Burm. f. *ponderosa* Hort. R. YAMAMOTO and Y. OSHIMA (J. Agric. Chem. Soc. Japan, 1931, 7, 312—319).—Citronin, $\text{C}_{28}\text{H}_{34}\text{O}_{14}$, m. p. 235° (Ac derivative, m. p. 132°), (yield 0.13%), when heated in a sealed tube with EtOH and H_3PO_4 , afforded citronetin, $\text{C}_{16}\text{H}_{14}\text{O}_5$, m. p. 204° (Me₂ ether, m. p. 125°), the sugar fraction of which contains rhamnose and glucose (equimol.). Citronin is 5-hydroxy-2'-methoxy-flavanone-7-rhamnoglucoside.

CHEMICAL ABSTRACTS.

Glucoside from Portuguese laurel, *Cerasus lusitanica*, Lois. H. HÉRISSEY and J. LAFOREST (Compt. rend., 1932, 194, 1095—1097).—*Lusitanicoside* crystallises from EtOAc in needles (m. p. 187—188°, $[\alpha]_D -74.69^\circ$) and does not contain N. It is hydrolysed by 2.5 wt.-% H_2SO_4 at 100° in 3½ hr. to give a dextrorotatory substance, but only slowly by emulsin. An enzyme prep. from laurel leaves hydrolyses it at room temp. in 5 days, giving a laevorotatory saccharide. Pentoses are not formed either by acid or enzymic hydrolysis.

P. G. MARSHALL.

Proteins of grasses. I. E. J. MILLER and A. C. CHIBNALL (Biochem. J., 1932, 26, 392—402).—The protein preps. have a low N content (12.3—14%) and contain varying amounts of N-free impurities which are difficult to remove. The NH_2 -acid composition of a prep. containing 14% N was very similar to that of other leaf-proteins; cystine could not be demonstrated, although the protein contained 1.0% S. Another prep. containing 0.75% S gave only small amounts of inorg. S, suggesting the presence of a non-basic S-containing NH_2 -acid.

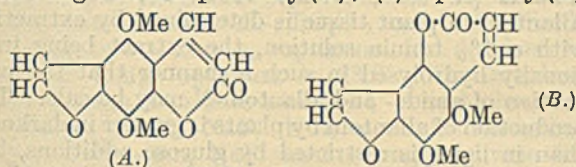
S. S. ZILVA.

Glyceride fatty acids of forage grasses. I. Cocksfoot and perennial ryegrass. J. A. B. SMITH and A. C. CHIBNALL (Biochem. J., 1932, 26, 218—234).—The fatty acids from cocksfoot and ryegrass are mainly unsaturated, saturated acids (palmitic and stearic) being present to the extent of 6 and 12% of the mixed acids, respectively. The presence of α -linolenic and α -linoleic acids is shown by Br addition and oxidation to OH-acids, but no oleic acid is found. Thiocyanometric analysis, which indicates the presence of oleic acid, is discussed critically.

A. COHEN.

Constituents of the root of *Pimpinella saxifraga*. I. F. WESSELY and F. KALLAB (Monatsh., 1932, 59, 161—174).—The light petroleum extract of the root contains pimpinellin (I) (cf. A., 1898, i, 598; 1908, i, 905), $\text{C}_{13}\text{H}_{10}\text{O}_5$, m. p. 119° (sinters at 117°), isopimpinellin (II), m. p. 151° (sinters at 148°), and a substance (still being investigated) closely allied to

(I) and (II). (I) and (II) both contain a lactone and two OMe groups. Reduction of (I) with Na-Hg gives (after distillation) *dihydropimpinellin* (III), m. p. 87—88° (slight previous sintering), converted by Me_2SO_4 and aq. KOH into an *acid* (IV), $\text{C}_{10}\text{H}_6\text{O}(\text{OMe})_2\text{CO}_2\text{H}$, m. p. 119°. Similar reduction of (II) affords a *hydroxy-acid*, m. p. 141° (sinters from 130°), converted by distillation into *dihydroisopimpinellin*, m. p. 99.5°, and by treatment with diazomethane (and subsequent hydrolysis) into (IV). Me_2SO_4 and alkali transform (I) and (II) into the same *acid*, $\text{C}_{10}\text{H}_4\text{O}(\text{OMe})_2\text{CO}_2\text{H}$, m. p. 162° (sinters at 143—156°), reduced by Na-Hg to (IV). Oxidation of (III) with HNO_3 gives $(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, whilst (I), (II), (III), bergapten, and xanthotoxin are all oxidised by alkaline H_2O_2 to furan-2:3-dicarboxylic acid. Reduction of the quinone obtained by Thoms (A., 1912, i, 40; 1913, i, 192) from aminobergapten, with SO_2 in H_2O at 90—95° and methylation of the resultant quinol with Et_2O -MeOH diazomethane gives (II), indicating that it is probably (A); (I) is probably (B).



H. BURTON.

Plant chemistry. XXIII. Chemistry of barks. VIII. C. G. DANOFF and J. ZELLNER (Monatsh., 1932, 59, 307—313).—The unsaponifiable matter of the material (2.75% of dry matter) extracted by light petroleum from the bark of the mountain ash (*Sorbus aucuparia*, L.) contains ceryl alcohol (I) and a *substance* (II), $\text{C}_{35}\text{H}_{60}\text{O}$ (termed *sorbicortol* I), m. p. 193°; the hydrolysate contains stearic acid. The unsaponifiable matter of the Et_2O -sol. matter (7.12%) consists of (I), (II), and *sorbicortol* II, $\text{C}_{16}\text{H}_{30}\text{O}_2$, m. p. 263°, α -28.9° in EtOH (crystallographic data given) (*benzoate*, m. p. 145°); amorphous resin acids are isolated from the hydrolysate. The EtOH extract contains phlobaphens, tannin, invert sugar, and (probably) choline. The dry material contains H_2O -sol. material (18.26%), sol. polysaccharide (0.37%), invert sugar (0.41%), tannin (4.47%), total N (1.55%), crude protein (9.72%), ash (4.62%), crude fibre (42.27%), pentosans (11.24%), and methyl-pentosans (1.16%).

The Et_2O -sol. material from the chestnut (*Castanea sativa*, Mill.) gives (on hydrolysis) phytosterol and higher fatty acids; the EtOH extract contains phlobaphens, tannin, and an unusually large amount of invert sugar.

H. BURTON.

Chemistry of lichens. I. *Peltigera canina*. J. ZELLNER (Monatsh., 1932, 59, 300—304).—The unsaponifiable matter of the light petroleum-sol. fraction of the residue from the COMe_2 extract of the lichen consists mainly of ergosterol. The petroleum-insol. material is separated by Et_2O and aq. KHCO_3 into (a) Et_2O -sol., (b) aq. extract, and (c) an insol. ppt., from which the following are isolated: (a) ergosterol, (b) a trace of an acid, and (c) a phenolic compound, m. p. 158° (sinters at about 150°), which may be identical with peltigerin (Zopf, A., 1909, i, 237).

Further extraction of the COMe_2 -treated material with EtOH affords mannitol and (after hydrolysis) ergosterol as the only recognisable products. The aq. extract of the lichen contains the K derivative of a substance similar to viscosin, small amounts of amorphous polysaccharides, H_2SO_4 , H_3PO_4 , and $\text{H}_2\text{C}_2\text{O}_4$, but no tannin.

H. BURTON.

Chemistry of halophytes. III. J. ZELLNER (Monatsh., 1932, 59, 305—306).—Details are given for the separation of betaine and a pectin-like carbohydrate from the aq. extract of *Suaeda salsa*, Pall.; tannins and a little invert sugar are also present.

H. BURTON.

Process of accumulation of oil and other principal nutritious substances in the grain of flax for fibre and for seed. M. P. ARCHANGELSKI and V. N. SUCHKINA (Bull. Appl. Bot., Russia, 1931, 25, 199—219).—During ripening the daily increase in org. matter and the wt. finally reached are greater in flax grown for seed than in that grown for fibre. The composition of the oil is the same, but is different from that of the oil of immature seed.

CHEMICAL ABSTRACTS.

Properties of plant substances in relation to climate and habitat—volatile oils, saponins, cyanogenetic glucosides, and carbohydrates. J. B. McNAIR (Amer. J. Bot., 1932, 19, 168—193).—Acids, alcohols, esters, and hydrocarbon constituents of volatile oils, saponins, and carbohydrates in plants from temperate regions have higher mol. wts. than those of tropical origin. *d*-Compounds predominate in temperate oils and *l*-compounds in tropical oils. Tropical saponins are less toxic to mice and to trypanosomes than those from temperate areas. Among the hydrolytic products of cyanogenetic glucosides COMe_2 is more general in those of temperate climates and PhCHO in tropical plants. Starches from temperate plants are very reactive, have a wide range of polarisation vals., higher gelatinisation temp., and are less "saturated" towards I than tropical plant starches.

A. G. POLLARD.

Composition of the seed of oleiferous plants in relation to geographical distribution. N. N. IVANOV, M. N. LAVROVA, and M. P. GAPOCHKO (Bull. Appl. Bot., Russia, 1931, 25, 1—86).—In general the oil content of a particular plant decreases from northerly to southerly latitudes. Increasing soil- H_2O increases the oil content and, for flax, the I val. of the oil.

CHEMICAL ABSTRACTS.

Constituents of essential oil in *Asarum*, Sieboldi, var. *seoulensis*, Nakai. T. KAKU, T. KONDO, C. CHO, and T. ORITA (Keijo J. Med., 1931, 2, 566—572).—The oil obtained by steam-distillation (yield 2.21%) had d_4^{25} 0.9988, $[\alpha]_D^{25}$ -0.75°, n_D^{20} 1.5141, sap. val. 28.4 (after acetylation 56.1), and acid val. 28.4. Constituents included palmitic acid, a phenol, $\text{C}_{10}\text{H}_{10}\text{O}_4$ (0.51%), *l*- β -pinene, saffrole, methyleugenol (47%), and eucarvone.

F. O. HOWITT.

Occurrence of iodine in fruits of *Feijoa sellowiana*, Berg. L. V. SERGEEV (Bull. Appl. Bot., Russia, 1931, 25, 279—288).—An irregularly high H_2O -sol. I content is recorded.

CHEMICAL ABSTRACTS.

Physiological effects of boron on wheat. H. S. MORRIS (Bull. Torrey Bot. Club, 1931, 58, 1—30).— $\text{Na}_2\text{B}_4\text{O}_7$, H_3BO_3 , or $\text{K}_2\text{B}_4\text{O}_7$ was toxic in concns. >0.005 g. of B per litre; except at high concns. of FeSO_4 neither Ca nor Fe reduced the toxicity. The alkali borates, but not H_3BO_3 , stimulate growth at concns. between 0.003 and 0.0005 g. of B per litre. With $\text{Na}_2\text{B}_4\text{O}_7$ and H_3BO_3 on wheat, differences attributed to p_{H} were observed.

CHEMICAL ABSTRACTS.

***Rauwolfia serpentina*, Benth.** L. VAN ITALLIE and A. J. STEENHAUER (Pharm. Weekblad, 1932, 69, 334—348).—Three alkaloids have been isolated from the root; that present in greatest quantity (*rauwolfine*) resembles in properties and reactions the ajmaline of Siddiqui (this vol., 203), but has the formula $\text{C}_{21}\text{H}_{26}\text{O}_2\text{N}_2$, m. p. 160° , $[\alpha]_{\text{D}} +13.1^\circ$ (hydrochloride, m. p. 130 — 140° , $[\alpha]_{\text{D}} +96.6^\circ$). The other two alkaloids (not characterised) have m. p. 262° and m. p. 177° , $[\alpha]_{\text{D}} -76.4^\circ$, respectively.

S. I. LEVY.

Millet proteins. H. ITO (Res. Bull. Gifu Imp. Coll. Agric., 1931, No. 17, 1—68).—The albumin, globulin, glutelin, and prolamine were isolated from *Panicum miliaceum*, *P. Crus-galli* var. *frumentaceum*, and *Setaria italica*; the properties and NH_2 -acid-N distribution were compared. CHEMICAL ABSTRACTS.

Influence of ageing on the alkaloid content of poppy capsules. C. BRAGA (Arch. Farm. sperim., 1931, 53, 255—260).—Ripe capsules of *Papaver somniferum* do not lose in alkaloid content during ageing. During ripening, the alkaloids of the narcotine and codeine group increase in amount at the expense of the morphine. Incision of the capsule does not influence the alkaloid content. T. H. POPE.

Fluctuations in the alkaloid content of the lupin. N. N. IVANOV and M. N. LAVROVA (Bull. Appl. Bot., Russia, 1931, 25, 291—302).—The total N content varied from 4.0 to 6.1% for *Lupinus angustifolius* and from 5.4 to 7.3% for *L. luteus*; the alkaloid content was parallel to the N content.

CHEMICAL ABSTRACTS.

Alkaloids of *Archangelisia flava* (L.), Merr. A. C. SANTOS (Univ. Philippines Nat. Appl. Sci. Bull., 1931, 1, 153—161).—The principal alkaloid is berberine; small quantities of jatrorrhizine, columbamine, and shobakunine were isolated.

CHEMICAL ABSTRACTS.

Alkaloids of *Pheanthus ebracteolatus* (Presl), Merrill. Pheanthine. I. A. C. SANTOS (Rev. Filipina Méd. Farm., 1931, 22, No. 9, 11 pp.).—At least 2 alkaloids are present. *Pheanthine*, $\text{C}_{34}\text{H}_{38}\text{O}_6\text{N}_2$, m. p. 210° , $[\alpha]_{\text{D}}^{20} -278^\circ$ in CHCl_3 [hydroiodide, m. p. 268° ; picrate, m. p. 263° ; chloroaurate, m. p. 170 — 171° ; chloroplatinate, m. p. 280° (decomp.)], contains 3 OMe and 2 NMe groups, but no OH, CO, or CH_2O groups or lactone structure. The structure is probably based on a tetrahydroisoquinoline ring system. (See this vol., 472.) CHEMICAL ABSTRACTS.

Alkaloids of *Argemone alba*, Lestib. P. A. FOOTE (J. Amer. Pharm. Assoc., 1932, 21, 246—248).—The dried overground portions of the flowering plant contain 2.63% (stems 3.25%) of alkaloid consisting principally of berberine. A small quantity of

an alkaloid giving a picrate, m. p. 232 — 235° , was isolated. Berberine was the only alkaloid found in the root. E. H. SHARPLES.

Isolation of sparteine from *Lupinus barbiger* (Watson). J. F. COUCH (J. Amer. Chem. Soc., 1932, 54, 1691—1692).—The light petroleum-sol. alkaloids from the leaves and stems of *L. barbiger* contain sparteine, isolated as the mercurichloride. Evidence for the presence of lupinine is not obtained. Two or three other alkaloids are present. C. J. WEST (b).

Fats of brown sea-weeds. B. RUSSELL-WELLS (Nature, 1932, 129, 654—655).—In the series *Pelvetia libera*, *P. canaliculata*, *Fucus vesiculosus*, and *Laminaria digitata* which grow at increasing depths, the fat content decreases with an increase in depth of immersion whilst that of the unsaponifiable residue increases; the general character of the fats is approx. the same. L. S. THEOBALD.

Origin of allantoin in plants. H. PURUCKER (Planta [Z. wiss. Biol.], 1932, 16, 277—331).—Allantoin in plant tissue is determined by extraction with a 4% tannin solution, the extract being fractionally hydrolysed in such a manner that the proportion of amide- and allantoin-N may be calc. The production of allantoin by plants is greater in darkness than in light, is restricted by glucose additions, but not appreciably affected by CHCl_3 narcosis. Allantoin is produced by the oxidation of purines and uric acid. The latter is not an intermediate product of purine oxidation, but is itself oxidised in several stages, one of which involves the formation of urea. Plants containing allantoin are characterised by cell-sap contents of high p_{H} in which purine degradation ceases with the formation of allantoin. The function of allantoin in plants is not that of counteracting NH_3 -poisoning. A. G. POLLARD.

Relation of life to electricity. VII. Stainability and electromotive forces in tissues which do not depend on acid-base combination. R. BEUTNER (Protoplasma, 1932, 15, 1—14).—Differential staining of cuticular and parenchymatous tissue, e.g., in the apple, is not related to acid-base combinations previously described (A., 1931, 1451) but to differences in partition coeffs. and other factors.

A. G. POLLARD.

Absorption and accumulation of solutes by living plant cells. I. Conditions which determine salt absorption by storage tissue. F. C. STEWARD (Protoplasma, 1932, 15, 29—58).—The accumulation of Br' in the sap of sliced potato tubers during immersion in aq. KBr is dependent on the maintenance of a high O_2 and low CO_2 concn. in the medium. Accumulation ceases at 5—6°. The extent of the accumulation is unaffected by illumination, but is markedly influenced by agitation. A logarithmic relationship exists between the internal and external Br' concns. Br' does not replace Cl' in the tissue to any appreciable extent. Absorption of both K' and Br' was considerable, but over any given time interval that of K was the greater. Freshly cut tissue immersed in salt solutions rapidly loses relatively large proportions of K and Mg and smaller amounts of Ca. These appear to be combined with org. anions. Dur-

ing the subsequent accumulation of K^+ and Br^- the internal concn. of Ca and Mg changed but little. The absorbed Br^- is in true solution in the cell-sap. In aerated solutions the time required to attain equilibrium between KBr solution and cell-sap may exceed 100 hr. A. G. POLLARD.

Genetical and biochemical aspects of anthocyan pigments. M. W. ONSLOW (Nature, 1932, 129, 601—604).—A review. L. S. THEOBALD.

Tormentol in several species of *Potentilla*, L. P. GILLOT and H. WIOLAND (Bull. Soc. Chim. biol., 1932, 14, 313—316).—Tormentol found in *P. tormentilla* (A., 1915, i, 83) occurs also in *P. anserina* and *P. reptans*, but not in *P. verna*. A. LAWSON.

Enzyme and salt-ions. III. Saccharogen-amylose of the leaves of differently nourished potatoes. G. VON DOBY and E. SZLADITS (Z. physiol. Chem., 1932, 206, 177—186; cf. A., 1931, 876).—The saccharogen-amylose of the leaves of potatoes grown on differently fertilised soil, viz., (a) unfertilised, (b) K-fertilised, and (c) K^+ , PO_4^{3-} , and Ca-fertilised, was compared. The p_H optimum for amylose is 6.75, the temp. optimum is 38.8°. The amylose concn. always decreases with age; it is highest on (a). Salts (NaCl, NaF, KCl) activate according to the fertilisation, NaF most strongly in case (a) at 0.001M; in case (c) at 0.1M it inhibits. Autolysis in case (a) increases the amylose activity up to 40% above normal on the 4th day; in the other cases the amylose activity falls from the 1st day. Salts, particularly NaF, augment the action of autolysis. J. H. BIRKINSHAW.

Constituents of gums. I. Gum arabic. E. PFAU (Apoth.-Ztg., 1931, 46, 724—725; Chem. Zentr., 1931, ii, 3218).—Gum arabic consists of 0.8% of NH_2 -acid (as salt), 2.6% of ash, a small quantity of carbohydrate, and a substance which is regarded as a connecting link between cellulose and carbohydrate (approx. 21% of galactose + 75% of arabinose). L. S. THEOBALD.

Oil from the fruit of *Melia azedarach*, L. L. E. HARRIS and R. M. WILSON (J. Amer. Pharm. Assoc., 1932, 21, 242—244).—Extraction of the ground fruit with light petroleum gave 7.38% of oil having d_{25}^{25} 0.9218, I val. (Hanus) 73.1, sap. val. 188.3, acid val. 3.5, and unsaponifiable matter 1.1%. The fatty acids contained oleic, linoleic, linolenic, and probably myristic and lauric or palmitic acids. E. S. SHARPLES.

Interrelation between substances in plants: essential oils and resins, cyanogen and oxalate. J. B. McNAIR (Amer. J. Bot., 1932, 19, 255—271).—Essential oils, resins, and CaC_2O_4 occur in twice as many species of tropical plants as in temperate ones. Essential oils and resins are found in similar anatomical structures and the constituents of the oils form resins by polymerisation or condensation. In plants CaC_2O_4 occurs in both mono- and tri-hydrated crystals, the latter predominating in temperate climates. Plants containing cyanogenetic glucosides also produce CaC_2O_4 in practically all instances. A. G. POLLARD.

Resin of *Ipomoea*. L. E. WARREN (J. Amer. Pharm. Assoc., 1932, 21, 217—223).—The charac-

teristics of 15 specimens of resin from *I. orizabensis*, Ledenois, ranged between the following limits: H_2O 0.65—5.25%, ash 0.07—1.03%, acid val. 8—18, sap. val. 171—195, ester val. 160—190, H_2O -sol. 0.22—7.49%, Et_2O -sol. 58—96%, $EtOH$ -insol. 0.015—2.76% (13 < 1%), light petroleum-sol. 1.70—3.48%. E. H. SHARPLES.

Croton-seed. II. Vesicant principle. E. CHERBULIEZ, E. EHNINGER, and K. BERNHARD (Helv. Chim. Acta, 1932, 15, 658—670).—The vesicant principle is obtained as a pale-coloured resin by extraction of croton-seed oil or of a MeOH extract of the seed with a mixture of Et_2O or light petroleum (b. p. 65—70°) with aq. MeOH (90%) or C_5H_5N ; 0.05—0.1% is thus obtained from the oil and 1—2.8% from the total seed. No loss of the vesicant properties occurs during its isolation. The product is unsaturated and has alcoholic properties; its vesicant properties are destroyed by bromination and considerably lessened by acetylation in the cold. Measurements of $[\alpha]_D^{25}$, I val., and Ac val. indicate that it is a mixture. It is not the cause of the purgative properties of the oil. H. A. PIGGOTT.

Significance of the occurrence of saponins for the systematic botany of varieties of *Clematis*. E. GILG and P. N. SCHÜRHOFF (Arch. Pharm., 1932, 270, 217—223).—Prantl's subdivision of the genus *Clematis* is in the main supported by the presence or absence of saponins. R. S. CAHN.

Poisonous constituent of *Coriaria intermedia*, Matsumura. J. MARANON (Philippine J. Sci., 1932, 47, 359—367).—The poisonous constituent of this shrub (which contains also gallic acid) is coriamyrtin. This substance, $C_{15}H_{18}O_5$, m. p. 218°, $[\alpha]_D^{25}$ -42.68° (in EtOH) (colour reactions described), reduces Fehling's solution after hydrolysis by acid, but is not a glucoside. R. S. CAHN.

Iron content of vegetables and fruits. H. K. STIEBELING (U.S. Dept. Agric., Circ. No. 205, 1932, 19 pp.).—Many original and published analyses of 110 different parts and varieties of vegetables and fruit show that most Fe is contained in potatoes and chlorophyll-containing parts of plants, but fruits on the whole are poor sources of this metal. E. B. HUGHES.

Unequal manganese contents of green and of etiolated leaves. G. BERTRAND and (MME.) M. ROSENBLATT (Compt. rend., 1932, 194, 1405—1408).—In a no. of vegetables examined, etiolated leaves contained less Mn than green leaves of the same species and variety. W. O. KERMACK.

Membranes of spores and pollens. VI. Determination of the polyamide-bitumens of brown and mineral coals. VIII. Pollenin from a brown coal. F. ZETSCHE and O. KÄLIN (Helv. Chim. Acta, 1932, 15, 412—431, 457—464).—VI. Sporin is estimated by measuring the increase in wt. on bromination, nitration, and oxidation. Lange-sporin, treated thus, is stable at room temp. and very sensitive to bases, by which it is debrominated. Fusin was determined by measuring its increase in wt. on conversion from its NO_2 - into its bromonitro-form. The polyamide-bitumens of

substances of varying stages of carbonisation, ranging from peat to mineral coal, were determined by treatment with Br and HNO_3 , washing the residue with HNO_3 , EtOH, and Et_2O , and, after drying over P_2O_5 , weighing. If the coal contains cellulose, treatment with H_3PO_4 is necessary. The stages in the natural carbonisation of the raw materials cellulose, lignin, fat, etc. are discussed.

VIII. Comparison of the empirical formulæ of pollenin, obtained from a brown coal and from *Pinus sylvestris*, bothrodendrin, obtained from a later brown coal, Lange-sporonin from a mineral coal, and tasmanin from an oil shale, shows that the process of carbonisation is accompanied by dehydration which may be followed by the addition of H_2 or S; in the former case an oil-shale results, in the latter a brown coal which loses H_2S to form an older brown coal. This loses H_2O , H_2S , and H_2 to form a mineral coal. A high S and OH-group content corresponds with easy oxidation by conc. HNO_3 . H. DAVSON.

Changes in root-tips of wheat and maize grown in mutual solutions deficient in calcium. R. BAMFORD (Bull. Torrey Bot. Club, 1931, 58, 149—178).—The injury is described. In the absence of Ca, other constituents of the culture solution, and especially Mg, are highly toxic to the root cells.

CHEMICAL ABSTRACTS.

Growth and variability of wheat seedlings in magnesium sulphate solutions. J. CARMIN (Bull. Torrey Bot. Club, 1931, 58, 179—190).—

CHEMICAL ABSTRACTS.

Magnesium injury of wheat. S. F. TRELEASE and H. M. TRELEASE (Bull. Torrey Bot. Club, 1931, 58, 127—148).—Injury of wheat, oats, rye, or barley seedlings grown in culture solutions containing 0.01—0.0025M-MgCl₂ is decreased or suppressed by addition of Ca or Sr.

CHEMICAL ABSTRACTS.

Action of arsenic on leaves. I. A. PARFENTIEF and W. K. DEVRENT (J. Pharm. Exp. Ther., 1932, 44, 171—189).—A cut bean-leaf, after immersion in H_2O , loses aq. vapour at the same rate as an uncut one immersed in 0.1% aq. As_2O_3 , showing that the toxic action of As is due to the prevention of utilisation of H_2O by the cells. The conductivity to H_2O of the vessels and the plasmolytic activity of the cells are unimpaired by treatment with As. The extracts obtained by immersing leaves in As solutions contain a hexose which is believed to be combined with As_2O_3 . The toxic action of As on leaves is ascribed to the decomp. of glucosides to form a complex with As.

H. DAVSON.

Toxicity of sodium nitrate for a species of moss. A. B. BEAUMONT (Science, 1932, 75, 312—313).—Chilean NaNO_3 is toxic to *Polytrichum commune*. KNO_3 , KCl, and NaCl are also toxic but not $\text{Ca}(\text{NO}_3)_2$, urea, $(\text{NH}_4)_2\text{SO}_4$, or Ca cyanamide.

L. S. THEOBALD.

Toxic substance in mulberry leaves damaged by tobacco. T. YABUTA and T. KOZU (J. Agric. Chem. Soc. Japan, 1931, 7, 932—941).—Leaves of mulberry, growing near tobacco, were toxic for the silk-worm owing to the presence of nicotine (1 in 10⁵).

CHEMICAL ABSTRACTS.

Assimilation of potato plants infected with leaf-roll. D. MÜLLER (Planta, [Z. wiss. Biol.], 1932, 16, 10—16).—The reduced dry matter production of diseased plants is partly or wholly the outcome of reduced assimilation intensity. A. G. POLLARD.

Use of celloidin in botanical technique. R. H. WETMORE (Stain Tech., 1932, 7, 37—62).

Titration of sugar with de Jong's reagent. N. SCHOORL (Pharm. Weekblad, 1932, 69, 253—255).—De Jong's method (this vol., 295) is accurate to within 5% if air is prevented from reaching the solution by keeping the liquid boiling. S. I. LEVY.

Determination of sugars in plant extracts. T. G. PHILLIPS (J. Biol. Chem., 1932, 95, 735—742).—EtOH extracts of plants were freed from EtOH, the aq. suspensions cleared with neutral $\text{Pb}(\text{OAc})_2$, and excess of Pb was removed by $\text{Na}_2\text{C}_2\text{O}_4$. The sugar contents of the resulting solutions were determined by methods employing reduction of Cu salts. For amounts of glucose less than 5 mg. a modified Fehling's method (A., 1922, ii, 92) is not satisfactory. No one reagent of those used is suitable for every type of plant extract. The corrections for sucrose vals. as given by glucose determinations before and after inversion were investigated. F. O. HOWITT.

Determination of amides in presence of carbohydrates. F. BAERTS and P. DELVAUX (Bull. Soc. Chim. biol., 1932, 14, 224—228).—The method of Schulze for the determination of amide-N does not give accurate results due to the partial decomp. of glutamine and asparagine in the $\text{NH}_2\text{-N}$ determination, and to the combination of fructose with the liberated NH_3 in the total-N determination. The loss of N in the second case increases as the duration of hydrolysis and the amounts of sugar and acid present increase. A. LAWSON.

Nephelometric micro-method for determination of cholesterol. O. MÜHLBOCK, C. KAUFMANN and H. WOLFF (Biochem. Z., 1932, 246, 229—246).—Bloor's method is recommended as being most trustworthy. A nephelometric micro-method for the determination of free and combined cholesterol in serum, blood, and organs is described.

P. W. CLUTTERBUCK.

Sero-diagnosis in foodstuff investigations. C. GRIEBEL and H. MAASS (Z. Unters. Lebensm., 1932, 63, 166—176).—Sp. anti-sera were prepared by defatting ground seeds with Et_2O and removing sugars in EtOH, followed by extraction of the residue with physiological saline. The filtered and diluted extract was then injected into dogs (2—5 c.c. in 2—4 days) and the anti-serum collected. Almond or apricot stones yielded sera which were sp. for both of these substances, but it was not possible either by means of the precipitin test itself or by fractional pptn. of the resulting deposits to distinguish between them. Sp. sera were obtained for hazelnut and groundnut and for anacardium (cashew nut) and pine seeds but not for walnut. The method has been applied successfully to the detection of ground hazels, pine, and anacardium seeds among hazels in chocolate. J. GRANT.

