General, Physical, and Inorganic Chemistry.

Intensity distribution in continuous bands of H_2. L. GOLDSTEIN (Compt. rend., 1931, **193**, 485—488). C. A. SILBERRAD.

Intensities of Balmer emission lines in stellar spectra. O. STRUVE and H. F. SCHWEDE (Physical Rev., 1931, [ii], **38**, 1195—1204). N. M. BLIGH.

Resonance spectrum of hydrogen. K. R. RAO and J. S. BADAMI (Nature, 1931, **128**, 585).—The peculiar distribution of intensity of the Lyman series of H obtained by the Paschen hollow-cathode discharge in He and As is interpreted as a resonance effect occurring only in the presence of As. L. S. THEOBALD.

Striations and magnetic effect in electrodeless discharges. J. T. TYKOCINER and J. KUNZ (Physical Rev., 1930, [ii], **35**, 1436). L. S. THEOBALD.

Excitation of the visible spectrum of helium. II. J. S. TOWNSEND and F. L. JONES (Phil. Mag., 1931, [vii], **12**, 815—823; cf. this vol., 539).—The variation of intensity with pressure in the visible spectrum of a high-frequency discharge in He was investigated. H. J. EMELÉUS.

Zeeman effect in ortho–helium band spectrum. J. S. MILLIS (Physical Rev., 1931, [ii], **38**, 1148—1163).—Resolved and partly resolved Zeeman patterns obtained at high dispersion agree with theoretical predictions for small rotational energy vals. Departures from predictions are discussed. N. M. BLIGH.

Band spectra of negative ions. R. MECKE (Z. Physik, 1931, **72**, 155—162).—The rule that mols. with like numbers and configurations of valency electrons have similar spectra indicates that bands in the BeH and MgH spark spectra are due to negative ions. Data for many hydrides suggest that the elastic vibration const. is characteristic only of the number and configuration of electrons forming the chemical linking, and this fits the conception of single, double, and triple linkings. A. B. D. CASSIE.

Properties of the third positive carbon and associated bands. J. KAPLAN (Physical Rev., 1930, [ii], **36**, 784).—The third positive group of CO and the two systems usually associated with it have been studied under different excitation conditions. L. S. THEOBALD.

New spectra in nitrogen. J. J. HOPFIELD (Physical Rev., 1930, [ii], **36**, 789).—With He as a source of continuous light, absorption band spectra of N_2 have been found in the region 600—1100 Å. The bands below 750 Å. form approx. Rydberg series

with 18·6 volts as the common limit. In a N_2–He mixture the resonance series of N I has been extended and a strong continuous spectrum has been found at the series limit; details of a new system of bands in emission are also given. L. S. THEOBALD.

Quenching of mercury resonance radiation by nitrogen and carbon monoxide. J. KAPLAN (Physical Rev., 1930, [ii], **36**, 788).—The more effective quenching power of CO is discussed. L. S. THEOBALD.

Active nitrogen glow. R. RUEDY (Physical Rev., 1930, [ii], **35**, 125).—A discussion. L. S. THEOBALD.

Third order spectrum of oxygen : quintuplets and triplets of O III. J. GILLES (Compt. rend., 1031, **193**, 584—586). C. A. SILBERRAD.

New oxygen spectra in the ultra-violet. J. J. HOPFIELD (Physical Rev., 1930, [ii], **36**, 789).—The resonance series of at. O has been extended and a strong continuous spectrum found to set in at the series limit and extend towards the ultra-violet. Many new lines, probably due mainly to O_1, have been found in O_2 and O_2–He mixtures. L. S. THEOBALD.

Rotational analysis of the first negative group of oxygen (O_2^+) bands. D. S. STEVENS (Physical Rev., 1931, [ii], **38**, 1292—1311).—Full data are tabulated. N. M. BLIGH.

New absorption band of atmospheric oxygen and the vibrational frequency of the normal molecule. H. D. BABCOCK (Physical Rev., 1930, [ii], **35**, 125).—30 lines of the absorption band (1, 1) in atm. O_2 have been identified. The most probable val. of the vibrational frequency of the normal mol. having 1 unit of vibrational energy is 1556·31 $\pm$0·05 cm.$^{-1}$ This val. is compared with the Raman displacement and discussed in connexion with isotopic displacement and heat of dissociation. L. S. THEOBALD.

Zeeman effect of neon. K. MURAKAWA and T. IWAMA (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1931, **16**, 256—259; cf. A., 1930, 1227).—Using improved methods, results previously reported are corrected and extended. N. M. BLIGH.

Intensity measurements in neon spectrum. H. N. SWENSON (Physical Rev., 1930, [ii], **35**, 126). L. S. THEOBALD.

Vectorial photo-electric effect in thin films of alkali metals. H. E. IVES (Physical Rev., 1931, [ii], **38**, 1209—1218). N. M. BLIGH.

Temperature shift of spectral lines and pole effect in vacuum arc. F. T. HOLMES (Physical Rev., 1930, [ii], 35, 652—653). L. S. THEOBALD.

Absorption of sodium vapour in the extreme ultra-violet. S. A. KORFF and J. L. NICKERSON (Physical Rev., 1930, [ii], 35, 1433).—Na vapour is practically transparent to radiation in the region 1300—300 Å. L. S. THEOBALD.

Ultra-violet light reflecting properties of aluminium. A. H. TAYLOR and J. D. EDWARDS (J. Opt. Soc. Amer., 1931, 21, 677—684).—Detailed directions are given for etching Al so as to obtain max. reflectivity. Reflexion factors range from 82 to 87% for visible light and from 81 to 82% for ultra-violet. C. W. GIBBY.

New bands in the sulphur spectrum. W. E. CURTIS and S. TOLANSKY (Proc. Durham Phil. Soc., 1931, 8, 323—331).—The relevant data for emission bands of S_2 vapour and visual estimates of the intensity are tabulated. Two types are encountered, strong and weak; these are analysed into vibrational progressions and compared with existing data. The weak system arises from a second electron transition having the same lower level as the strong system. W. R. ANGUS.

Sparking potential of A-NO mixtures. F. M. PENNING (Z. Physik, 1931, 72, 338—343).—NO lowers the sparking potential of A provided the electrodes are previously saturated with NO (cf. A., 1928, 214). A. B. D. CASSIE.

Intensity relations in some of the stronger multiplets of Cr I and Cr II. C. E. HESTHAL (Physical Rev., 1930, [ii], 35, 126). L. S. THEOBALD.

Classification of iron lines. H. D. BABCOCK (Physical Rev., 1930, [ii], 36, 784—785). L. S. THEOBALD.

Interferometric measurements in the spectrum of the iron arc in air in the region 3100—3500 Å. C. V. JACKSON (Proc. Roy. Soc., 1931, A, 133, 553—564).—A set of 46 lines in the spectrum of the Fe arc in air, in the region 3100—3500 Å., has been measured by interferometric comparison with the red line of Cd or the Fe secondary standards. L. L. BIRCUMSHAW.

Resonance spectrum of diatomic molecules of selenium and tellurium. P. SWINGS and J. GENARD (Bull. Acad. roy. Belg., 1931, [v], 17, 1099—1106).—A criticism of the work of Kessel (Compt. rend. Soc. polon. Phys., 1931, 5, 409) on the resonance spectra of Se_2 and Te_2. W. R. ANGUS.

Vibrational quantum analysis of the visible absorption bands of bromine. W. G. BROWN (Physical Rev., 1931, [ii], 38, 1179—1186).—The absorption bands from 5100 to 7600 Å. are classified into two band systems having a common lower level; one system includes previously recorded bands, the other a group of relatively weak bands in the extreme red. Measurements of the vibrational isotope effect are given for bands in the main system, leading to a revision of quantum numbering and vibrational consts. N. M. BLIGH.

Hyperfine structures in the first spectra of krypton and xenon. C. J. HUMPHREYS (Bur. Stand. J. Res., 1931, 7, 453—463).—The stronger arc lines of Kr and Xe have been analysed. R. CUTHILL.

Spark spectrum of rhodium. A. G. SHENSTONE and J. J. LIVINGOOD (Physical Rev., 1930, [ii], 36, 380).—New terms in the first spark spectrum of Rh are given. L. S. THEOBALD.

Effect of low temperatures on the ultra-violet transmission band of silver. J. C. McLENNAN, C. E. SMITH, and J. O. WILHELM (Phil. Mag., 1931, [vii], 12, 833—840).—The position of max. intensity in the ultra-violet transmission band of a Ag film was determined at the temp. of liquid air, H_2, and He. H. J. EMELÉUS.

Bands of silver hydride. E. BENGTSSON and E. OLSSON (Z. Physik, 1931, 72, 163—176).—New bands between 3180 and 4700 Å. give the energy of dissociation of the ground state as 19,000 cm.$^{-1}$ A. B. D. CASSIE.

Voltage-intensity relations of the cadmium spectra. D. COLSON (Physical Rev., 1930, [ii], 35, 294).—Crit. potentials of the more prominent arc and spark lines are given and their behaviour as a function of the energy of the imparting electron is traced. L. S. THEOBALD.

Spectrum of singly-ionised indium. R. J. LANG (Physical Rev., 1930, [ii], 35, 126).—The deepest term corresponds with an ionisation potential of 18·81 volts. L. S. THEOBALD.

Multiplet structure and Zeeman effect. J. B. GREEN and R. A. LORING (Physical Rev., 1931, [ii], 38, 1289—1291).—The relations deduced by Houston and by Goudsmit (cf. A., 1930, 971) applied to the Zeeman effect of Sn III and Sb I give results in good agreement with observed vals. N. M. BLIGH.

Spectra of trebly- and quadruply-ionised antimony, Sb IV and Sb V. J. S. BADAMI (Proc. Physical Soc., 1931, 43, 538—544).—A study of the spark spectrum of Sb under various conditions of excitation. A. B. D. CASSIE.

Infra-red absorption band system of iodine. W. G. BROWN (Physical Rev., 1931, [ii], 38, 1187—1189).—A vibrational analysis is given for a weak band group in the region 8300—9300 Å. of the absorption spectrum of saturated I vapour between 80° and 150°; the system is analogous to the extreme red of Br. A region of continuous absorption having a max. at 7320 ± 50 Å. was observed. N. M. BLIGH.

Iodine fluorescence in the infra-red. F. W. LOOMIS (Physical Rev., 1930, [ii], 35, 662).—When the yellow lines are filtered from the Hg arc the lines in the neighbourhood of the infra-red doublets of the fluorescence spectrum of I disappear. They should therefore be attributed to higher members of the fluorescence series excited by the yellow lines. L. S. THEOBALD.

Arc spectrum of iodine. S. F. EVANS (Proc. Roy. Soc., 1931, A, 133, 417—430).—The arc spectrum of I has been photographed over the region 4763—10,481 Å. Wave-lengths are tabulated

and a term scheme is proposed which accounts for the majority of the strong arc lines. The ionisation potential, calc. from the deepest term $5p^2P_{3'2} = 84{,}560$ cm.$^{-1}$, is 10·44 volts. L. L. Bircumshaw.

Hyperfine structure and Zeeman effect in the resonance lines of Ba II. R. Ritschel and R. A. Sawyer (Z. Physik, 1931, **72**, 36—41).—The 4934 and 4554 Å. lines of Ba II were investigated with fields up to 2600 gauss ; the components observed are in agreement with the isotopes 136 and 138 having no nuclear spin, and the 137 isotope having some spin. A. B. D. Cassie.

M-Series absorption spectrum of tantalum. C. A. Whitmer (Physical Rev., 1931, [ii], **38**, 1164—1169).—Spectrograms were obtained for 3 absorption limits at 5·64 (M_{III}), 6·773 (M_{IV}), and 6·997 (M_V) Å. Discrepancies between experimental ν/R vals. and those calc. from L absorption and emission data are discussed. N. M. Bligh.

Magnetic resolution and nuclear moment of rhenium. P. Zeeman, J. H. Gisolf, and T. L. de Bruin (Nature, 1931, **128**, 637).—Data obtained for the arc and under-water spark spectra of Re are discussed. The nuclear moment of Re is 5/2. L. S. Theobald.

High-frequency spectrum of mercury and fine structures of λ 6123 (Hg I) and λ 4797 (Hg II). S. Tolansky (Proc. Physical Soc., 1931, **43**, 545—553).—Intensity modifications in the high-frequency electrodeless discharge in Hg vapour near 0·001 mm. are explained by the electron excitation curves. The 6123 and 4797 Å. lines were investigated with a Fabry–Perot interferometer. A. B. D. Cassie.

Mercury band spectrum in fluorescence. (Lord) Rayleigh (Nature, 1931, **128**, 724—725).—Three bands, originally found in absorption by Wood, occur at 2345, 2338, and 2334 Å. when Hg vapour saturated at 5 mm. pressure is excited to fluorescence by a cooled Hg vac. arc. the light of which is filtered by a dil. solution of thiophen in EtOH. L. S. Theobald.

Hyperfine structure of mercury. K. Murakawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **16**, 243—255).—The hyperfine structure and Paschen–Back effect of the Hg line λ 4046·5 are described. The Paschen–Back effect determines uniquely the nuclear moment of all the Hg isotopes : $I=0$ for even isotopes, 1/2 for Hg^{199}, and 3/2 for Hg^{201}. N. M. Bligh.

Relative intensities of arc and spark lines of the electrodeless discharge in mercury vapour. O. P. Hart and O. Stuhlman, jun. (Physical Rev., 1930, [ii], **35**, 1437). L. S. Theobald.

High-frequency electrodeless discharge characteristics. O. Stuhlman, jun., M. D. Whitaker, and M. L. Braun (Physical Rev., 1930, [ii], **35**, 1436—1437). L. S. Theobald.

Near infra-red spectrum of mercury. H. J. Unger (Physical Rev., 1930, [ii], **36**, 784).—Several lines in the region 1—2 μ have been resolved into 2 or more lines. L. S. Theobald.

Electrodeless discharge in mercury vapour. H. Smith, W. A. Lynch, and N. Hilberry (Physical Rev., 1930, [ii], **36**, 374). L. S. Theobald.

Paschen–Back effect in the hyperfine structure of thallium II. J. B. Green and J. Wulff (Z. Physik, 1931, **71**, 593—599).—Zeeman components in the 3092 Å. Tl II lines were measured for the fields 14,700, 32,500, and 43,350 gauss, and are in agreement with theory. A. B. D. Cassie.

Hyperfine structure in Tl II. Relative g (I) factors of Tl, Bi, and Pb (207), and nuclear structure. J. C. McLennan, A. B. McLay, and M. F. Crawford (Proc. Roy. Soc., 1931, **A, 113**, 652—667).—The status of the theory of hyperfine structure separation is considered. Certain conclusions regarding nuclear structure are reached by comparing the observed vals. of the interaction consts. of certain s electrons of Tl, Bi, and Pb. The fact that the g (I) factors of Bi and Pb (207) are of the same order, whereas that of Tl is about four times as great, invalidates the assumption that the resultant moments of momentum of nuclei are entirely due to spinning protons. L. L. Bircumshaw.

Appearance of continuous spectra during cathode-ray bombardment. IV. Experiments with thorium and other elements in gases. W. M. Cohn (Z. Physik, 1931, **72**, 392—422). —Th, U, and Po when exposed to electron bombardment in presence of gases at low pressures exhibit a blue or violet surface luminosity which is continuous and unpolarised. A. B. D. Cassie.

Colorimetric properties of the spectrum. J. Guild (Phil. Trans., 1931, **A, 230**, 149—187).—The colorimetric properties of the eye have been averaged for 7 observers. A standard for a " normal " eye in colorimetry is suggested. J. W. Smith.

Coupled duplet and octet. A. F. Richter (Phil. Mag., 1931, [vii], **12**, 764—768).—The ionisation potential curves and chemical properties of certain elements are explained in terms of the neutralisation of residual moments, and coupling. H. J. Emeléus.

Origin of the line absorption spectra of the rare earths. O. Laporte (Physical Rev., 1930, [ii], **35**, 130).—Theoretical. L. S. Theobald.

Excitation of the green auroral line. J. Kaplan (Nature, 1931, **128**, 304). L. S. Theobald.

Space-charged Townsend discharge in dense clouds. W. Deutsch (Ann. Physik, 1931, [v], **10**, 847—867).—Charging of suspended particles in an ionic atm. is determined and the effect of surrounding particles taken into account. A. B. D. Cassie.

Pauli exclusion principle. W. Heisenberg (Ann. Physik, 1931, [v], **10**, 888—904).—At. systems requiring n electrons to complete a closed shell can be approx. investigated by a Schrödinger equation in the co-ordinates of the n " missing " electrons. The method is used to discuss the lowest terms of at. spectra, such as Ti and Ni, and O^{++} and O; the anomalous Hall effect provides another example. A. B. D. Cassie.

Perturbation in band spectra. G. P. Ittmann (Z. Physik, 1931, **71**, 616—626).—Theoretical.
　　　　　　　　　　　　　　A. B. D. Cassie.

Allowed levels for equivalent (s, p, d, f) electrons with (j j) coupling. S. D. Bryden, jun. (Physical Rev., 1931, [ii], **38**, 1145—1147).—Allowed levels are tabulated.　　　　N. M. Bligh.

Plasma-electron resonance, plasma resonance, and plasma shape. L. Tonks (Physical Rev., 1931, [ii], **38**, 1219—1233; cf. this vol., 888).
　　　　　　　　　　　　　　N. M. Bligh.

Generalisation of the Rydberg formula. R. M. Langer (Physical Rev., 1930, [ii], **35**, 649—650).
　　　　　　　　　　　　　　L. S. Theobald.

Quantitative application of the irregular doublet law to an isoelectronic sequence. R. A. Sawyer and J. E. Mack (Physical Rev., 1930, [ii], **35**, 661).　　　　　　　L. S. Theobald.

Energy distribution in the ultra-violet spectrum of skylight. B. O'Brien (Physical Rev., 1930, [ii], **36**, 381).　　　　　　L. S. Theobald.

Calculation of ionic spectra. E. Fermi (Mem. R. Accad. Ital., Sci. Fis. Mat. Nat., 1930, **1**, Fis., No. 2, 8 pp.; Chem. Zentr., 1931, i, 2845).—Theoretical.　　　　　　A. A. Eldridge.

Apparatus for the evaluation of absorption [and line] spectrograms. G. W. Kühl (Chem. Fabr., 1931, 373—374).—The distances between the lines or absorption edges on the spectrograms are amplified mechanically and read on a scale which may be calibrated in wave-lengths or wave numbers.
　　　　　　　　　　　　　　H. F. Gillbe.

Absolute measurement of certain X-ray wave-lengths. J. M. Cork (Physical Rev., 1930, [ii], **35**, 128).—An X-ray vac. spectrograph and glass grating have been used to obtain abs. wave-lengths of the elements from Mo to Sb.　　　L. S. Theobald.

Ionisation of inert gases (except helium) by X-rays. O. Gaertner (Ann. Physik, 1931, [v], **10**, 825—832).—The energy absorbed per pair of ions formed when X-rays of wave-length 1·27 X traverses Ne is 43, A 29, Kr 32, and Xe 47·5 volts. For shorter wave-lengths A gave 28—29 volts.
　　　　　　　　　　　　　　A. B. D. Cassie.

Incoherent scattering of X-rays. W. Heisenberg (Physikal. Z., 1931, **32**, 737—740).—Mathematical.　　　　　　　　J. W. Smith.

Incoherent scattering of X-rays. L. Bewilogua (Physikal. Z., 1931, **32**, 740—744).—The theoretical curves for the incoherent scattering of X-rays, calc. according to the method of Heisenberg (cf. preceding abstract), are compared with experimental data.　　　　　　　J. W. Smith.

Interference of X-rays in thin layers. H. Kiessig (Ann. Physik, 1931, [v], **10**, 769—788; cf. A., 1930, 1334).—Interference of X-rays reflected at the upper and lower surfaces of a thin layer of Ni on a glass plate was observed; separation of the fringes gives vals. of the layer thickness and its refractive index.　　　　　　　A. B. D. Cassie.

Atomic photo-electric effect in the K shell according to Dirac's relativistic wave mechanics.

F. Sauter (Ann. Physik, 1931, [v], **11**, 454—488; cf. this vol., 994).—Mathematical.　　J. W. Smith.

Satellites of $K\alpha$ for the elements nickel to arsenic. F. K. Richtmyer and E. Ramberg (Physical Rev., 1930, [ii], **35**, 661).　　L. S. Theobald.

Excitation of the $L\alpha$ satellites of silver. S. W. Barnes and F. K. Richtmyer (Physical Rev., 1930, [ii], **35**, 661).　　　　　L. S. Theobald.

Multiple ionisation and secondary X-ray absorption edges. A. Sandström (Nature, 1931, **128**, 759).—Multiple ionisation in X-ray spectra has been confirmed by finding a secondary edge in S at 4644·0 X.
　　　　　　　　　　　　　　L. S. Theobald.

Apparatus for measuring absorption coefficients of soft X-rays in gases and the absorption in air of the $K\alpha$ line of carbon. E. Dershem and M. Schein (Physical Rev., 1930, [ii], **36**, 378).
　　　　　　　　　　　　　　L. S. Theobald.

Modified line in scattered X-rays. P. A. Ross and J. C. Clark (Physical Rev., 1930, [ii], **36**, 378).—No step structure or breadth of line inexplicable by lack of homogeneity of scattering angle has been detected in the scattering of Sb $K\alpha_1$ and $K\alpha_2$ from Be at angles between 55° and 75°.　L. S. Theobald.

X-Ray absorption by a Thomas–Fermi atom. L. C. Roess and E. H. Kennard (Physical Rev., 1931, [ii], **38**, 1263—1269).—The calc. ionisation potential for a K electron of Sn shows approx. agreement with the observed energy of the K absorption edge.　　　　　　　　N. M. Bligh.

Dependence of Compton line breadth on primary wave-length with the multi-crystal spectrograph. J. W. M. Du Mond and H. A. Kirkpatrick (Physical Rev., 1931, [ii], **38**, 1094—1108; cf. this vol., 405).—The breadth of the Compton line diminished with shorter primary wave-lengths in accordance with Du Mond's theory.
　　　　　　　　　　　　　　N. M. Bligh.

Index of refraction and absorption coefficient of gold for the $K\alpha$ line of carbon. E. Dershem (Physical Rev., 1930, [ii], **35**, 128).—The reflexion intensity–glancing angle curve for sputtered Au and the $K\alpha$ line of C (44·6 Å.) has been obtained. The extinction coeff. is 0·0086 and $1-n=0·009$.
　　　　　　　　　　　　　　L. S. Theobald.

Atmospheric ionisation at Glencree, Co. Wicklow. J. J. Nolan and P. J. Nolan (Proc. Roy. Irish Acad., 1931, **40**, 11—59).—Data for observations extending over 14 months are tabulated. The concentration of condensation nuclei varied from 40 to 43,000 per c.c.; the average vals. for positive and negative ions were 495 and 369, respectively. The effects of rain and diurnal variations were noted. An expression for the rate of production of ions is found.
　　　　　　　　　　　　　　N. M. Bligh.

Ionisation of cæsium vapour by light. F. W. Cooke (Physical Rev., 1931, [ii], **38**, 1351—1356).—The photo-ionisation of Cs vapour as a function of the wave-length of the light was measured at low pressure and plotted. The abs. val. of the at. ionisation coeff. at the series limit was 6×10^{-19}.
　　　　　　　　　　　　　　N. M. Bligh.

Emission of positive ions from thoriated tungsten. H. B. WAHLIN (Physical Rev., 1930, [ii], 35, 653).—On heating, thoriated W gives W ions of mass 184, Th ions of mass 232, and an ion of mass 247 ± 2. The last appears at approx. 2300° and may be ThO or an element.   L. S. THEOBALD.

Photo-electric effect and the J phenomenon. T. H. OSGOOD (Physical Rev., 1930, [ii], 35, 1407).—A discussion.   L. S. THEOBALD.

Photo-electric properties of extremely thin films of alkali metals. H. E. IVES and H. B. BRIGGS (Physical Rev., 1930, [ii], 35, 669; cf. A., 1925, ii, 344).   L. S. THEOBALD.

Effect of adsorbed thorium on the thermionic emission from tungsten. W. H. BRATTAIN (Physical Rev., 1930, [ii], 35, 1431).—Deposition of Th on a W ribbon at a given temp. increases thermionic emission to a max. and then decreases it to a stationary val.   L. S. THEOBALD.

Ionisation efficiency of electrons in potassium vapour. J. KUNZ and A. HUMMEL (Physical Rev., 1930, [ii], 35, 123).   L. S. THEOBALD.

Inhibition of photo-electric emission by near infra-red light. A. R. OLPIN (Physical Rev., 1930, [ii], 36, 376).—The response of K photo-electric cells to white light is increased when small amounts of Br or I vapour are distilled on to the cathodic surface. A marked decrease in the photo-electric current then occurs when the cell is irradiated with infra-red light.   L. S. THEOBALD.

Search for critical potentials for electron recombination with Hg^+. A. M. CRAVATH (Physical Rev., 1930, [ii], 35, 659—660).—No effect due to recombination of 10·4-volt electrons with Hg^+ could be detected.   L. S. THEOBALD.

Direct measurement of the velocity of cathode rays. C. T. PERRY and E. L. CHAFFEE (Physical Rev., 1930, [ii], 35, 1437).   L. S. THEOBALD.

Mathematical equivalence of two ways of regarding the excitation of an atom by a fast-moving electron. J. W. FRAME (Proc. Camb. Phil. Soc., 1931, 27, 511—517).

Wentzel–Brillouin approximation method in wave mechanics, particularly for the hydrogen molecule ion. (FRL.) M. WILLSTÄTTER (Ann. Physik, 1931, [v], 10, 873—887).—Mathematical.   A. B. D. CASSIE.

Diffraction and brake-effect of electrons. A. SOMMERFELD (Ann. Physik, 1931, [v], 11, 257—330). —Mathematical.   W. R. ANGUS.

Release of secondary electrons by means of hydrogen canal rays in metals. G. SCHNEIDER (Ann. Physik, 1931, [v], 11, 357—384).—The apparatus and technique are discussed. The no. and velocity of secondary electrons released by the bombardment of thin plates of Al and Au by H canal rays have been measured.   W. R. ANGUS.

Electronic emission from a metal target bombarded with positive ions. C. L. UTTERBACK and W. GEER (Physical Rev., 1930, [ii], 36, 785—786).   L. S. THEOBALD.

Scattering of high-velocity electrons by thin foils. H. V. NEHER (Physical Rev., 1931, [ii], 38, 1321—1341).—Scattering by thin foils of Al, Ag, and Au was investigated as a function of primary energy, at. no., and angle. Elimination of secondary electrons was effected.   N. M. BLIGH.

Capture and loss of electrons by helium ions in helium. P. RUDNICK (Physical Rev., 1931, [ii], 38, 1342—1350).—Mean free paths for capture and loss were measured, using an ion source giving strictly homogeneous velocities. Results are compared with available data and with information on ionisation and energy loss.   N. M. BLIGH.

Elastic scattering of slow electrons in gases. II. E. C. BULLARD and H. S. W. MASSEY (Proc. Roy. Soc., 1931, A, 133, 637—651).—The angular distributions of slow electrons scattered elastically in He, Ne, N_2, H_2, and CH_4 have been measured over the range 20—125°, using the apparatus previously described (this vol., 542). The results are interpreted in terms of the quantum theory of electron scattering. The effects due to the field of the atom, the distortion of the incident wave by the at. field, and the exchange of electrons between the atom and the colliding beam are discussed. For heavy atoms the second factor is of chief importance, whereas for light atoms the effect of exchange predominates.   L. L. BIRCUMSHAW.

Diffraction of electrons in gases. F. L. ARNOT (Proc. Roy. Soc., 1931, A, 133, 615—636).—The angular distributions of the elastically scattered electrons in Xe, Kr, A, Ne, H_2, N_2, CH_4, and CO have been measured for velocities of the primary beam between 30 and 800 volts. The lower-velocity curves of the rare gases all show distinct diffraction patterns, whilst those of the mol. gases have a min. at about 90°. At the higher velocities the max. and min. have practically disappeared in the cases of Kr and Xe, and have completely disappeared in the other gases. The angular distribution curves have been used to determine the effective cross-section curves for elastic collisions; these give information concerning the variation with velocity of the proportion of elastic to inelastic collisions. The similarity of the angular scattering curves and the cross-section curves of CH_4 and H_2 may be accounted for by assuming that the electrons in CH_4 are scattered mainly by the four H_2 nuclei of the CH_4 mol. It may be possible to examine the structure of complex mols. by analysis of the diffraction patterns in the angular scattering curves.   L. L. BIRCUMSHAW.

Photo-electrons and negative ions. E. M. WELLISH (Nature, 1931, 128, 547—548).—A summary of experiments on the formation of negative ions from electrons. The majority of negative ions appear to be formed near the electrode at which the electrons originate, and electrons which do not give rise to negative ions near this electrode in general cross the interval between the electrodes in the free condition.   L. S. THEOBALD.

Secondary emission from nickel by impact of metastable atoms and positive ions of helium. M. C. HARRINGTON (Physical Rev., 1931, [ii], 38, 1312—1320; cf. A., 1930, 1336).   N. M. BLIGH.

Recombination of ions in air and oxygen in relation to the nature of gaseous ions. O. Luhr (Physical Rev., 1930, [ii], 36, 787; cf. this vol., 783). — L. S. Theobald.

Properties of natural H-rays. C. Pavlovski (Ann. Physique, 1931, [x], 16, 150—195).—Natural H-rays have been obtained by the action of α-rays from Po on H_2, paraffin, cellophane, and collodion, the scintillation method, Wilson's method, and the chamber method having been used in their measurement. The max. range is 4·1 times the range of the α-particles used; thus the H-rays are produced by the elastic collision of an α-particle with an H nucleus, but the number of H-rays diminishes with diminishing speed of the α-rays, contrary to the theory of elastic collisions. The H-ray emission of a substance depends only on its H content, other atoms causing no modification of the effect. J. W. Smith.

Action of positive ions of cæsium on a hot nickel surface. P. B. Moon (Proc. Camb. Phil. Soc., 1931, 27, 570—577).—The emission of secondary electrons from hot Ni surfaces bombarded by Cs⁺ ions at normal incidence increased with increasing energy of the primary ions and diminished with rise of target temp. W. R. Angus.

Recombination of electrons with cæsium ions. E. H. Kurth (Physical Rev., 1930, [ii], 36, 374).— No positive effect was observed under the conditions employed. L. S. Theobald.

Excitation of spectral lines by collision of slowly moving positive ions. A. Günther-Schulze and F. Keller (Z. Physik, 1931, 72, 143—154).—Spectra due to He, Ne, A, Kr, H_2, O_2, and N_2 were excited by positive ions of 200—700 volts energy. A. B. D. Cassie.

Scattering of atoms. S. Mizushima (Physikal. Z., 1931, 32, 789—803).—Mathematical. Angular distributions are calc. for scattering of light atoms by heavy atoms, and of atoms by atoms of comparable mass. A. B. D. Cassie.

Mobilities of gaseous ions in chlorine and chlorine–air mixtures. L. B. Loeb (Physical Rev., 1930, [ii], 35, 137).—Mobilities in Cl_2 on the new abs. standard for positive and negative ions are 0·654 and 0·510 cm. per sec. per volt per cm., respectively. Traces of Cl_2 (<0·1%) in dry air reduce the negative mobility below that of the positive ion, which is little affected by the presence of Cl_2. L. S. Theobald.

Cross-section of argon with respect to argon⁺. F. Wolf (Z. Physik, 1931, 72, 42—53).—The cross-section of A to an A positive ion remains const., and greater than the gas kinetic cross-section, up to 520 volts, when a steady increase begins. A. B. D. Cassie.

Specular reflexion of atoms from crystals. A. Ellett (Physical Rev., 1930, [ii], 35, 293; cf. this vol., 14).—Theoretical. L. S. Theobald.

Mean free path of potassium atoms in nitrogen. J. J. Weigle and M. S. Plesset (Physical Rev., 1930, [ii], 36, 373—374).—Preliminary measurements give an average val. of $3—5 \times 10^{-9}$ for the mean free path of K atoms in 10^{-2} to 10^{-5} cm. pressure of N_2. L. S. Theobald.

Scattering of atomic hydrogen by gases : mercury, argon, oxygen, and iodine. E. G. Lunn and F. R. Bichowsky (Physical Rev., 1930, [ii], 35, 671).—The collision diameter of H atoms passing through gaseous Hg, A, O_2, or I is a property of the degree of interaction between the colliding particles. L. S. Theobald.

At. wt. of thallium. H. V. A. Briscoe, S. Kikuchi, and J. B. Peel (Proc. Roy. Soc., 1931, A, 133, 440—457).—Full details are given of a method, more rapid and precise than that of nephelometric titration, of titrating halides with Ag, and the method has been applied to the redetermination of the at. wt. of Tl by measurement of the ratio TlCl : Ag. The result Tl=204·34, with an average deviation of ±0·015, is in good agreement with the val. 204·39 (average deviation of ±0·012) given by Hönigschmid and Striebel (this vol., 141). Crookes' ratio, Tl : $TlNO_3$, is found to be unsuitable for determining the at. wt. Crookes' val. Tl=204·04 must therefore be abandoned. In the absence of any direct evidence by the positive-ray method as to the existence of isotopes of Tl, it is concluded that the fractional val. deduced for the at. wt. indicates that the element is probably a mixture of two or more isotopes. (Cf. Aston, this vol., 1349.) L. L. Bircumshaw.

Element 87. J. Papish and E. Wainer (J. Amer. Chem. Soc., 1931, 53, 3818—3820).—The product obtained by working up 10 kg. of samarskite to obtain a high concentration of Cs afforded X-ray lines appropriate to element 87 in the Moseley diagram. J. G. A. Griffiths.

Relative abundance of lithium isotopes. W. R. van Wijk (Naturwiss., 1931, 17, 894—895).—Sources of error in Schüler's calculation of the ratio of the relative abundance of Li isotopes (this vol., 1207) are discussed. The ratio is <10·5 and the author's val. of 7·2 (ibid., 992) is not precluded, although considerably less than Aston's val. of 10·2 (ibid., 994). W. R. Angus.

Isotope effect in the band spectrum of lithium hydride. G. Nakamura (Nature, 1931, 128, 759—760).—The isotope effect is clearly established for each strong line in the spectrum (A., 1930, 124) due to the less abundant Li⁶H mol. With a change in conditions the relative intensity of the isotope lines varies from 2 : 1 to 8 : 1 for the ratio Li⁷H : Li⁶H. L. S. Theobald.

Origin of O¹⁷. S. C. Lind (Physical Rev., 1930, [ii], 35, 1408).—Considerations are advanced showing it to be highly improbable that any important fraction of O¹⁷ in the atm. has been generated in the earth's crust or atm. by α-ray bombardment. L. S. Theobald.

Demonstration of the existence of isotopes of sulphur by analysis of the fine structure of the resonance spectrum of diatomic sulphur molecules. P. Swings (Bull. Acad. roy. Belg., 1931, [v], 17, 1095—1097).—The necessity for examining the absorption spectrum of S_2 with large dispersion in order to detect isotopic effects is advocated. W. R. Angus.

Chlorine isotope Cl³⁹. G. Hettner and J. Böhme (Z. Physik, 1931, 72, 95—101).—Vibration-rotation lines due to the HCl³⁹ mol. were detected in

the first harmonic at 1.76μ of the fundamental band, using the second-order spectrum of an echelette grating.
A. B. D. CASSIE.

Vibrational isotope effect. R. T. BIRGE (Physical Rev., 1930, [ii], **35**, 133).—Results for Cl_2 and ICl are discussed.
L. S. THEOBALD.

Nuclear moments of the isotopes of lead. Relative values of the g (I) factors of Pb^{207} and thallium. J. C. McLENNAN, M. F. CRAWFORD, and L. B. LEPPARD (Nature, 1931, **128**, 301).—Optical data show that the g (I) factor of the Tl nucleus is approx. 4 times that of the Pb^{207} nucleus. The moment of at least one of the nuclei is composite and not due simply to a spinning proton. This invalidates the rule that each proton contributes $\pm\frac{1}{2}h/2\pi$ to the resultant; some of the protons in one of the nuclei must be endowed with a property additional to spin.
L. S. THEOBALD.

Constitution of thallium and uranium. F. W. ASTON (Nature, 1931, **128**, 725).—Tl consists of two isotopes 203 and 205, the latter predominating to an extent in agreement with the accepted at. wt. (204·39). Mass spectra for UF_6 indicate that U is probably simple to at least 2 or 3%. The 238 line is strong, and is followed by a series 257 UF, 276 UF_2 . . . 333 UF_5, the last being the heaviest mass recorded on a mass spectrum.
L. S. THEOBALD.

Periodic system of atomic nuclei and the principle of regularity and continuity of series. W. D. HARKINS (Physical Rev., 1931, [ii], **38**, 1270—1288).—New relations and rules for the existence and stability of at. nuclei, and for the abundance and isotopic nos. of isotopes are given. The regularities of the He, U, Li, and Be series are plotted. The at., mass, isotopic, and electronic nos. of all known isotopes are recorded, and related to the periodicity of at. nuclei; undiscovered isotopes are predicted.
N. M. BLIGH.

Microneutrons. V. A. PLOTNIKOV (J. Gen. Chem. Russ., 1931, **1**, 446—454).—The difference between the at. wt. of He and of 4H amounts to 4×0.00724, representing 4 microneutrons, each consisting of one electron and one microproton; these would be liberated as energy in the condensation of 4 H atoms to form He.
R. TRUSZKOWSKI.

Periodicity of the atomic nucleus. R. SWINNE (Wiss. Veröff. Siemens-Konz., 1931, **10**, No. 4, 137—147).—Empirical relations have been derived between the degradation const. and at. wt. and no. of nuclear electrons of radioactive elements. The abundance of elements is discussed and results are extrapolated beyond U to a hypothetical trans-U, for which an especially long life period is to be expected.
J. W. SMITH.

Radioactive disintegration. A. BRAMLEY (Proc. Nat. Acad. Sci., 1931, **17**, 579—583).—An equation for nuclear energy levels has been developed and the wave-lengths of γ-rays deduced from it are compared with experimental vals. This equation also affords a means of calculating the mean life of a radioactive atom.
W. R. ANGUS.

Processes of ionisation by α-rays and their measurement by a Millikan condenser. G.
SCHMIDT (Z. Physik, 1931, **72**, 275—292).—The Millikan oil drop forms a convenient small electrometer for determination of ionisation at different points along an α-ray track; ionisation of the K-level in air was followed along a Po α-ray track.
A. B. D. CASSIE.

Analysis of α-particles emitted from thorium-C and actinium-C. (LORD) RUTHERFORD, C. E. WYNN-WILLIAMS, and W. B. LEWIS (Proc. Roy. Soc., 1931, A, **133**, 351—366).—Two distinct groups of long-range α-particles are emitted from Th-C, of ranges 9·781 and 11·662 cm. The question of their origin is discussed. Earlier conclusions on the complexity of the main group of α-particles (range about 5·4 cm.) from Ac-C have been confirmed (cf. A., 1930, 1338). No α-particles of range greater than 6·6 cm. have been found.
L. L. BIRCUMSHAW.

β-Particle emission of radium-D. H. O. W. RICHARDSON (Proc. Roy. Soc., 1931, A, **133**, 367—380).—The tracks formed by the β-particles of Ra-D have been photographed in a Wilson expansion chamber, and the ranges of 377 tracks have been measured, using a stereoscopic method. An energy distribution curve has been constructed for the particles emitted; the secondary electronic groups are identified in this distribution, and the extent to which the continuous spectrum is represented is discussed. An attempt has been made to estimate the abs. no. of particles emitted per disintegration.
L. L. BIRCUMSHAW.

Soft γ-rays from the active deposit of thorium. R. ARNOULT (Ann. Physique, 1931, [x], **16**, 196—207). —The results of Rutherford and Richardson (A., 1914, ii, 13) have been confirmed. In addition, a very readily absorbable radiation not reported by these authors has been detected. Disintegration of 100 atoms of Th-B produces about 80 quanta of radiation of wave-length 0·97 Å., 15 of 1·6 Å., and 260 of 4·6 Å.
J. W. SMITH.

Measurement of the intensity of γ-rays of radium in r-units. O. GLASSER and V. B. SEITZ (Physical Rev., 1930, [ii], **35**, 1432).
L. S. THEOBALD.

Complete dissociation of hydrogen. E. U. CONDON (Physical Rev., 1930, [ii], **35**, 658).—Theoretical.
L. S. THEOBALD.

Average life for ionised helium. L. R. MAXWELL (Physical Rev., 1930, [ii], **36**, 379).
L. S. THEOBALD.

Possibility of bringing mean life directly into the Schrödinger equation for the hydrogen atom. A. BRAMLEY and A. C. G. MITCHELL (Physical Rev., 1930, [ii], **35**, 1419).
L. S. THEOBALD.

Life and radius of the metastable mercury atom. M. L. POOL (Physical Rev., 1930, [ii], **35**, 1419).
L. S. THEOBALD.

Theory of excitation by collision with heavy particles. N. F. MOTT (Proc. Camb. Phil. Soc., 1931, **27**, 553—560).

Evaporation of glowing wires in a vacuum. I. L. PRÁSNIK (Z. Physik, 1931, **72**, 86—94).—Theoretical.
A. B. D. CASSIE.

Matter and radiation. F. G. DONNAN (Nature, 1931, **128**, 290—292).—A lecture.

L. S. THEOBALD.

Magnetic experiments on the cosmic rays. B. ROSSI (Nature, 1931, **128**, 300—301).

L. S. THEOBALD.

Nature of cosmic radiation. L. F. CURTISS (Physical Rev., 1930, [ii], **35**, 1433).—The application of a magnetic field to two Geiger–Müller tube counters decreases the no. of coincidences by 25%, an effect attributed to cosmic radiation, which is thus a corpuscular radiation of high energy.

L. S. THEOBALD.

Similarity between cosmic rays and gamma rays. R. A. MILLIKAN and I. S. BOWEN (Nature, 1931, **128**, 583).—The cause of the similar divergence from linearity in the pressure–ionisation curves of cosmic rays and the γ-rays of Ra and Th is discussed.

L. S. THEOBALD.

Absorption and dissociative or ionising effect of monochromatic radiation in an atmopshere on a rotating earth. II. S. CHAPMAN (Proc. Physical Soc., 1931, **43**, 483—501).

A. B. D. CASSIE.

Electrical charging of suspended particles. C. TRAGE (Ann. Physik, 1931, [v], **10**, 833—845).—A Wollaston wire replaced the suspended particle in a test of the gas kinetic theory of the charging of particles; the results are in agreement with Arendt and Kallmann's theory (cf. Z. Physik, 1926, **35**, 421).

A. B. D. CASSIE.

Angular momentum of light. (SIR) C. V. RAMAN (Nature, 1931, **128**, 545).

L. S. THEOBALD.

Spin of light quanta. (SIR) C. V. RAMAN and S. BHAGAVANTAM (Nature, 1931, **128**, 727).—Spectroscopic measurements of the depolarisation of scattered light in the case of CS_2 and C_6H_6 (by Venkateswaran) confirm the results predicted by the theory that photons possess intrinsic angular momentum.

L. S. THEOBALD.

Experiments with an automatic photo-electric spectrophotometer. P. J. MULDER and J. RAZEK (Physical Rev., 1930, [ii], **35**, 1424).—The instrument can be used for testing solutions which change colour rapidly. Records for hæmatin and oxyhæmoglobin solutions have been obtained. L. S. THEOBALD.

Analysis of complicated band spectra with the aid of magnetic rotation spectra. R. W. WOOD and G. H. DIEKE (Nature, 1931, **128**, 545—546).—The absorption spectrum of NO_2 is much simplified by the application of a magnetic field. The theoretical significance of magnetic rotation structure for diat. gases is discussed. L. S. THEOBALD.

Effect of magnetic field on absorption spectrum of nitrogen peroxide. P. LAMBERT and I. AGARBICEANU (Compt. rend., 1931, **193**, 732—733; cf. preceding abstract).—These effects are being investigated by means of the great electromagnet of Bellevue, and the sensitiveness of some lines to the magnetic field has been demonstrated.

C. A. SILBERRAD.

Secondary structure of lithium fluoride. T. H. JOHNSON (J. Franklin Inst., 1931, **212**, 507—514; cf.

A., 1930, 1232).—The reflexion of at. H from the cleaved (100) surface of a LiF crystal yields diffuse secondary spectra, and this phenomenon is regarded as evidence for a secondary structure on the surface, which may have the period required by Zwicky's theory (ibid., 139). N. H. HARTSHORNE.

Spectrum of barium fluoride in the extreme red and near infra-red. T. E. NEVIN (Proc. Physical Soc., 1931, **43**, 554—558).—The spectrum of BaF_2 was investigated between 6700 and 8700 Å.

A. B. D. CASSIE.

Ultra-violet bands of CO in the electrodeless ring discharge. H. P. KNAUSS and J. C. COTTON (Physical Rev., 1931, [ii], **38**, 1190—1194).—The relative intensities of bands in the region 2900—2150 Å. were observed, and compared with Geissler tube spectra. The Cameron bands including the 2157 Å. band appeared at low pressures; the bands of the CO^+ ion were strong at all pressures, and the fourth positive bands at high pressures. N. M. BLIGH.

Absorption spectra of some mercury and cadmium halides in the vapour phase. K. BUTKOW (Z. Physik, 1931, **71**, 678—688).—The absorption spectra of the vapours of HgI_2, CdI_2, and $HgBr_2$ were measured in the region 7000—1950 Å.; absorption maxima in the ultra-violet are associated with different modes of dissociation of the mol. The spectra are similar to those obtained from solutions, except for additional maxima obscured by the presence of a solvent. A. B. D. CASSIE.

Spectrum of potassium permanganate. F. VLÈS and A. SIMCHEN (Compt. rend., 1931, **193**, 581—584).—The visible and ultra-violet spectrum of $KMnO_4$ in buffered solution of p_H 8·7 consists of 21 bands in two groups, indicating two modes of mol. vibration. Some ten successive states of the MnO_4' ion are indicated. The moment of inertia is therefore dependent on the p_H (cf. A., 1930, 12).

C. A. SILBERRAD.

Absorption spectra of pure hydrochloric acid and of bromine in the ultra-violet. (MME.) N. DEMASSIEUX and V. HENRI (Compt. rend., 1931, **193**, 591—592).—The absorption spectrum in aq. HCl beyond λ 2500 is due to a trace of Br. Pure aq. HCl shows no absorption up to λ 2144. Br in aq. HCl shows an absorption ten times as strong as is shown by the same amount of Br in H_2O, whence it is inferred that a compound of Br and HCl is present, and that addition of aq. HCl should accelerate bromination (cf. A., 1913, ii, 690). C. A. SILBERRAD.

Absorption spectra of the alkyl halides; energies of the C–I and C–Br linkings. T. IREDALE and A. G. MILLS (Proc. Roy. Soc., 1930, **A**, **133**, 430—439).—The energies of the C–I and C–Br linkings, calc. from the heats of combustion of the alkyl iodides and bromides, are in good agreement with the spectroscopic energies calc. from the long-wave limits of the continuous absorption bands of the alkyl halides in the near ultra-violet. It is considered that the alkyl halides dissociate on absorption of light into alkyl residues and excited halogen atoms. The fact that the absorption limits shift towards the red when the alkyl halides are liquefied may be explained on

the basis of energy level changes due to mol. association.   L. L. Bircumshaw.

Transmission of ultra-violet radiation by lake water. C. D. Hodgman (Physical Rev., 1930, [ii], 35, 1423).—H_2O is rendered less transparent to ultra-violet radiation by the presence of small amounts of dissolved salts and org. substances such as occur in natural river and lake waters.   L. S. Theobald.

Mirror image correspondence of absorption and fluorescence spectra. I. V. L. Levschin (Z. Physik, 1931, 72, 368—381).—Between 20° and −70° fluorescence spectra are exact mirror images of absorption spectra; this holds for C_6H_6 as well as for coloured solutions, and is a fundamental property of luminescence.   A. B. D. Cassie.

Fluorescence spectrum of benzene. F. Almasy and C. V. Shapiro (Physical Rev., 1930, [ii], 35, 1422).—The fluorescence spectrum of C_6H_6 excited by a quartz Hg arc agrees with the absorption spectrum in the range where both overlap. Most of the bands can be accounted for by assuming that the electronic origin of the system lies at 37,489 cm.$^{-1}$ The vibrational frequencies are 923 cm.$^{-1}$ for the excited state and 998 and 160 cm.$^{-1}$ for the normal state.
                           L. S. Theobald.

Electronic transitions in the spectra of benzene. C. V. Shapiro, R. C. Gibbs, and J. R. Johnson (Physical Rev., 1930, [ii], 35, 1422).—Spectroscopic data for C_6H_6 show that only two electronic transitions, at 37,489 and 38,612 cm.$^{-1}$, need be assumed to provide an adequate energy level scheme. The fluorescence spectrum is confined to the first system, whilst the absorption spectrum is distributed between both. The Tesla luminescence spectrum is similar to that of fluorescence.   L. S. Theobald.

Band spectrum of benzene : existence of a small vibrational frequency in the normal state. C. V. Shapiro, R. C. Gibbs, and J. R. Johnson (Physical Rev., 1931, [ii], 38, 1170—1178).—A postulated vibrational frequency of 160 cm.$^{-1}$ is discussed, and is shown to be in agreement with theoretical deductions.   N. M. Bligh.

Determination of the structure of absorption resonators of organic chromophores. VIII. **Mechanism of the absorption of light and of shared-resonators.** IX. **Extinction curves of ωω′-diphenylpolyenes.** X. **Extinction curves of azines.** XI. **Structure of shared-resonators in anthracene, acridine, phenazine, phenanthrene, and pyrene.** XII. **Influence of mode of attachment on the frequency of a shared-resonator.** XIII. **Determination of the structure of the halochromic compounds of polyene hydrocarbons, quinones, and polyene ketones.** XIV. **Structure of the shared-resonators of polyene ketones.** D. Rădulescu (Ber., 1931, 64, [B], 2223—2225, 2225—2229, 2230—2233, 2233—2240, 2240—2242, 2243—2249, 2249—2250).—VIII. A polyene resonator is compared with a vibrating string made up of several similar components in which the tension and proper vibration of the elementary components can be individually varied. The properties of shared-resonators are expressed as follows. Tension

being kept const., the main frequencies of shared-resonators diminish with increase in the no. of elementary components. Powerful, polar-negative substituents cause marked diminution of the main frequencies; an even stronger effect is produced by the addition of strong positive charges to the electrons of the resonator. Mechanical strains and distortions of the mol. cause corresponding changes of the characteristic vibrations. The atoms united by these electrons undergo harmonic vibration during the vibrations of the shared-resonator, so that every frequency of a shared-resonator corresponds with a copulated, infra-red at. frequency. The light energy absorbed by the electrons in any given period is completely utilised by the at. structure and transformed into heat or potential energy.

IX. [With F. Bărbulescu.] Examination of the extinction curves of αδ-diphenylbutadiene, αζ-diphenylhexatriene, α0-diphenyloctatetraene, and αμ-diphenyldodecahexaene shows that the wave-length of the extinction max. increases with the no. of elementary components. At least 11 copulated elementary resonators (6 continuously conjugated double linkings) are necessary for the production of a pronounced crocetene spectrum. Two double linkings exhibit only a single structureless band, whereas with three, fission into bands is first noticed, which is well developed in diphenyloctatetraene without attaining the true crocetene structure.

X. [With V. Alexa.] The spectra of αδ-diphenylbutadiene, α0-diphenyloctatetraene, αμ-diphenyldodecahexaene, benzylidene-, cinnamylidene-, and ε-phenylpentadienylidene-azine are compared. Replacement of the C atoms by 2 N atoms caused marked change in the electric tension in three of the elementary resonators, since the shared-resonator is not made up of completely similar but of three types of components, C:C, C:N, and N:N, with atom-carrying pairs of differing polarity and, consequently, of differing tension. The heterogeneity of the components of the shared-resonator finds its expression in a partial obscuring of the characteristic spectrum of the resonator. Replacement of the C by N atoms in the resonator-carrier causes the individual bands to flow together, and a somewhat scattered shading of the band system of the initially homogeneous resonator results.

XI. [With G. Ostrogovich.] As predicted by the author's theories, the extinction curve of anthracene shows two well-marked peaks, a band spectrum of long wave-length of the crocetene or naphthacene type with several pronounced maxima corresponding with electromeride I_A and a short wave-length peak corresponding with a diffused C_6H_6 band and due to electromeride I_B. The extinction curve of phenanthrene is not similar to that of anthracene and there is absorption much further towards the ultra-violet. The acridine and phenazine spectra consist of two well-separated peaks, a long wave-length peak corresponding with a diffused anthracene peak and a short wave-length peak due to the C_6H_6 nuclei. The extinction curve of pyrene exhibits three peaks, anthracenoid, naphthalenoid, and belonging to an otherwise unknown, highly-unstabilised, two-membered resonator.

XII. [With G. Ostrogovich and F. Bărbulescu.]

The expected relationship between perylene and naphthacene is exhibited in their spectra, each of which consists of a long wave-length crocetenoid peak and a short wave-length naphthalenoid peak. With the former hydrocarbon the long wave-length peak is displaced towards the region of short wavelength and somewhat blurred in comparison with the latter hydrocarbon. The difference is ascribed to the mode of angulation, since it is also shown by pyrene and anthracene, the A forms of which possess the same number of elementary components; the spectrum of the angularly arranged resonator is strongly displaced towards the ultra-violet.

XIII. The extinction curves of polyenes (benzylideneacetophenone etc.) in EtOH and EtOH–HCl have been measured. The complexes which cause intense coloration are exclusively substances with a positive-polar central atom which have the tendency to fill the inner sphere with negative polar groups (NR_3, OR_3, etc.). It follows, therefore, that the polyene hydrocarbons must add with their negativepolar component in the inner sphere at the positive central atom. The sole negative component in a simple polyene chain is the elementary resonator (:), i.e., the electrons of the conjugated double linkings.

Such a complex, e.g., with $SnCl_4$, can correspond only with the general scheme (I). The immediate proximity of the strongly positive metallic ion causes an unusually pronounced loosening of the electron arrangement in the resonator and explains the marked deepening of the colour. In accordance with the octet theory, the Cl atom of $HClO_4$ must be unusually strongly polar-positive, thus explaining the formation of coloured complexes with polyenes of the same spectral character as those with $SnCl_4$. The coloured compounds given by many aromatic hydrocarbons with polynitro-compounds are considered to be formed by the attachment of their resonator electrons to the NO_2-group.

XIV. [With V. ALEXA.] The long wave-length absorption max. of polyene ketones is displaced in the direction of greater wave-length in the sequence Ph styryl, distyryl, Ph δ-phenyl-$\Delta^{\alpha\gamma}$-butadienyl, di-δ-phenyl $\Delta^{\alpha\gamma}$-butadienyl, and di-ζ-phenylhexatrienyl ketone. In addition to the long wave-length-maxima, shorter wave-length maxima occur corresponding with the not continuously conjugated electromerides. These correspond with the non-conjugated CO group ($COMe_2$), the group C:C:C:C in cinnamyl derivatives, and the group C:C:C:C:C hexadienyl compounds.
H. WREN.

Absorption of light and complex formation with unsaturated compounds. B. ARENDS (Ber., 1931, 64, [B], 1936—1951; cf. A., 1917, i, 261; 1919, ii, 40; 1923, ii, 201).—The absorption spectra of the following substances have been quantitatively examined: stilbene, isostilbene, α-methyl- and αβ-dimethyl-stilbene in EtOH; tetraphenylethane, tetraphenylethylene dichloride, stilbene, tri- and tetraphenylethylene in $CHCl_3$; cis-dichloro-, cis-dibromo-, and p-methyl-stilbene in EtOH; cinnamic acid, styrene, αβ-dichloro-β-phenylpropionic and β-phenyl-propionic acids in EtOH; cinnamic, allocinnamic, cis- and trans-dibromocinnamic acid in MeOH. The results are discussed in detail. The decomp. consts. of the following complex compounds have been examined by measurement of the changes of solubility in heterogeneous system and by photometric determination of the concentrations in homogeneous system: picric acid with stilbene, p-methyl-, p-chloro-, α-methyl-, phenyl-, dichloro-, and dibromo-stilbene, tetraphenylethylene, and dibenzyl. H. WREN.

Infra-red absorption of fused and crystalline quartz from 2 μ to 8 μ. F. E. McGINNETY (Proc. Durham Phil. Soc., 1931, 8, 337—350).—Available data on the absorption of fused and cryst. quartz have been collected, unified, and discussed.
W. R. ANGUS.

Infra-red absorption of hydrates. A. E. VAN ARKEL and C. P. FRITZIUS (Rec. trav. chim., 1931, 50, 1035—1045).—The distinction between hydrate and hydroxyl formation is discussed. The ability of a salt to form hydrates depends on the energy required to separate the ions sufficiently to permit a H_2O mol. to be inserted between them being greater than the energy gained by the effect of the H_2O dipole on the field of the ions, and this, in turn, depends on the ionic radii and charges. In the cases studied hydrates may be distinguished from OH-compounds by their infra-red spectra, which for the former show, like H_2O, bands at 1·5 and 2·0 μ, whilst those for the latter do not. N. H. HARTSHORNE.

Absorption of acetylene and ethylene in the near infra-red. R. M. BADGER (Physical Rev., 1930, [ii], 35, 1433).—Absorption spectra of C_2H_2 and C_2H_4 have been photographed in the region 6800—9200 Å. C_2H_2 has a band with sharp lines, showing marked intensity alternation, with centre at approx. 7886 Å.; C_2H_4 has a complex band, centre at approx. 8706 Å., which also shows convergence.
L. S. THEOBALD.

Infra-red absorption spectrum of carbonyl sulphide. C. R. BAILEY and A. B. D. CASSIE (Nature, 1931, 128, 637—638).—The absorption spectrum of COS, obtained by means of a monochromator method, has bands at 527*, 859, 1051, 1718*, 1898*, 2079, 2904, 3095*, 3742*, and 4084* cm.$^{-1}$ (* signifies relatively weak intensities). The results are discussed and a few P—R branch separations given. L. S. THEOBALD.

Technique of the Raman effect. P. GRASSMANN (Z. Physik, 1931, 72, 240—241).—Multiple reflexions can be used to give measurable Raman scattering from 0·1 c.c. of liquid. A. B. D. CASSIE.

Kinetics of fluctuations. M. LEONTOVITSCH (Z. Physik, 1931, 72, 247—265).—Mathematical. The results are applied to fine structure of lines due to scattering by solutions. A. B. D. CASSIE.

Raman effect in rock-salt. E. FERMI and F. RASETTI (Z. Physik, 1931, 71, 689—695).—The Raman effect of rock-salt is a weak continuous displacement extending to a limit at 365 cm.$^{-1}$ from the original line. Vibrations in rock-salt are symmetrical and to a first approximation should show no Raman effect; quadratic terms of the elastic dis-

placements must be included in the polarisability of the crystal to account for any Raman effect; this explains a limit at twice the residual ray frequency.

A. B. D. CASSIE.

Fine structure of Raman bands. I. Structure of carbon tetrachloride Raman bands and the symmetry of quadrivalent carbon. A. LANGSETH (Z. Physik, 1931, **72**, 350—367; cf. this vol., 1111).—Normal vibrations and isotope effects in molecules of type XCl_4 are discussed. Raman spectra due to CCl_4, $SnCl_4$, CBr_4, $POCl_3$, and SO_2Cl_2 were investigated with a dispersion of 8 Å. per mm.; the 458 cm.$^{-1}$ displacement in CCl_4 is a triplet, due to isotopes, and the 218 and 314 are doublets, probably due to C having C_3^v symmetry. A. B. D. CASSIE.

Structure of Raman band of water. G. BOLLA (Nature, 1931, **128**, 546—547).—Nine weak, diffuse components (wave-lengths given) have been observed in the Raman band of H_2O excited by the Hg line 2536 Å. at 17°. The average distance between two components is 50 cm.$^{-1}$ L. S. THEOBALD.

Structure of the Raman band of water. S. RAFALOWSKI (Nature, 1931, **128**, 546).—The Raman bands of H_2O become sharper with an increase in concentration of HNO_3 in its aq. solution; the central component divides into two, whilst the intensity of the short wave-length component increases rapidly. With HCl, the intensity of both outer components decreases with an increase in concentration, whilst the inner component apparently enlarges.

L. S. THEOBALD.

Raman lines due to co-ordination linking. D. M. BOSE and S. DATTA (Nature, 1931, **128**, 725—726; cf. this vol., 25).—A co-ordination linking is a weak valency linking between the central atom and one of the co-ordinated group and should manifest itself in the Raman spectra. The spectra of the Hg radiation scattered by solutions of $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_6]Cl_2$ give evidence of the presence of modified lines in the case of the cobaltic compound only. The former is a true co-ordination compound and the latter an associated compound.

L. S. THEOBALD.

Raman spectra of chloroform and silicochloroform. M. DE HEMPTINNE and (MLLE.) A. PEETERS (Bull. Acad. roy. Belg., 1931, [v], **17**, 1107—1118).—Raman displacements for $CHCl_3$ and $SiHCl_3$ are given and compared with existing data. Frequencies evaluated from force-const. formulæ are in good agreement with observed displacements. The displacement of 587 cm.$^{-1}$ is characteristic of the Si·Cl linking. W. R. ANGUS.

Raman effect in some acid derivatives and esters. V. N. THATTE and A. S. GANESAN (Phil. Mag., 1931, [vii], **12**, 823—832).—The Raman spectra of Ac_2O, mono-, di-, and tri-chloroacetic acids, isoamyl nitrate, allylthiocarbimide, $Et_2C_2O_4$, AcCl, and BzCl were measured and discussed. H. J. EMELÉUS.

Dispersion of polarisation of light scattering. K. S. KRISHNAN and A. SARCAR (Indian J. Physics, 1931, **6**, 193—205).—The dispersion of the polarisation of the light scattered by C_6H_6 has been measured by a method which is independent of the polarisation of the instrument. Measurements with liquid C_6H_6 extend-

ing to 3100 Å. give a const. val. for the depolarisation factor suggesting, presumably, const. optical anisotropy. W. R. ANGUS.

Intensity and polarisation of lines scattered by ring-shaped hydrocarbons. J. WEILER (Z. Physik, 1931, **72**, 206—214).—The 992, 803, 826, 886, and 905 cm.$^{-1}$ Raman lines of C_6H_6, C_6H_{12}, C_6H_{10}, C_5H_{10}, and of C_5H_8, respectively, are ascribed to radial vibrations, and the absence of the 1030 cm.$^{-1}$ line from C_6H_6 scattering indicates that this frequency is due to tangential vibration. A. B. D. CASSIE.

Angular distribution of intensity of Raman lines. D. P. RAY-CHAUDHURI (Z. Physik, 1931, **72**, 242—246).—The angular distribution of intensity of the Raman lines 4215, 4555, and 4617 Å. due to C_6H_6, using a Hg vapour lamp, obeyed the $(1+\cos^2\theta)$ law between 15° and 145°. A. B. D. CASSIE.

Raman effect. XIV. Raman spectrum of organic substances (nitro-compounds, nitrates, nitrites). A. DADIEU, F. JELE, and K. W. F. KOHLRAUSCH (Monatsh., 1931, **58**, 428—455).—Data are given for 34 different compounds, including aromatic and aliphatic NO_2-compounds, aliphatic nitrates and nitrites, inorg. nitrates and nitrites, and HNO_3. The lines 1340 and 1529 cm.$^{-1}$ appear to be characteristic of the NO_2-group in aromatic compounds, with the possible exception of o- and p-$BrC_6H_4\cdot NO_2$. In the aliphatic compounds the frequencies are a little higher and vary with the position of the NO_2-group. The org. nitrates have lines in the neighbourhood of 1274, 1627, 860, and 580. The org. nitrites have only one strong high frequency, 1635, and also one at 600. Several show exceptional features. The results are discussed with reference to the large dipole moment of the NO_2-group. The question of the presence of the ψ-acid form, $HO\cdot NO_2$, in HNO_3 is considered. M. S. BURR.

Raman spectra of liquid mixtures. P. KRISHNAMURTI (Nature, 1931, **128**, 639).—Dilution of AcOH to 95% introduces at 1712 cm.$^{-1}$ a new faint component to the line at 1667 cm.$^{-1}$ Further dilution increases intensity until at 75% acid only one broad line at 1712 cm.$^{-1}$ is present. The results indicate that $AcOH,H_2O$ is formed. L. S. THEOBALD.

Effect of temperature on fluorescence of dye solutions and some consequences of the law of mirror image correspondence. II. V. L. LEVSCHIN (Z. Physik, 1931, **72**, 382—391).—The effect of temp. for changes in intensity, width of spectral region, and the position of max. fluorescence relative to the max. of absorption was investigated. Quenching of fluorescence of solutions was also investigated.

A. B. D. CASSIE.

Energy transformations at surfaces. II. Photoluminescence of fluorescent dyes at surfaces. H. KAUTSKY, A. HIRSCH, and W. BAUMEISTER (Ber., 1931, **64**, [B], 2053—2059; cf. this vol., 1033).—According to their nature, the dyes are adsorbed on SiO_2 gel E or $Al(OH)_3$ gel. The adsorbates are washed with H_2O, heated for about 2 hr. at about 150°/high vac., and sealed in evacuated glass tubes. Fluorescence, similar to that of their solutions, occurs with all the adsorbates in daylight, particularly

with brightly fluorescing dyes (fluorescein, rhodamines, *iso*quinoline-red, acridines). Trypaflavine–SiO_2 gel adsorbates exhibit very marked phosphorescence initially very little weaker than the emission during irradiation, but declining rapidly. The property is shared by many other acridine dyes. The colour of the phosphorescence is similar to that of the fluorescence of corresponding adsorbates. (For the detection of very short phosphorescence a simple phosphoroscope is described.) Brightness and duration of phosphorescence are not connected with intensity of fluorescence. Duration is diminished greatly by rise in temp., but prolonged by powerful cooling and then accompanied by alteration in the nature of the emitted light in the direction of longer wave-length. A similar but less pronounced effect is observed with the fluorescence. With small concentration of dye the gel particles glow throughout their whole mass, whereas with greater concentrations the glow is restricted to the outer surface and displaced towards longer wave-length. Fluorescence is not markedly diminished in brightness, but the phosphorescence is greatly curtailed. Gel particles are much more highly fluorescent than equiv. droplets of aq. or EtOH solution.   H. WREN.

Chemiluminescence in oxidation of dyes and phenols by hydrogen peroxide and ferrous sulphate, or by ozone. N. N. BISWAS and N. R. DHAR (Z. anorg. Chem., 1931, **199**, 400—405).—The luminescence of various dyes and phenols is more marked in non-aq. solution than in aq. solution, and increases with rise in temp. With the dyes the luminescence diminishes as the concentration increases, whereas the reverse is true of the phenols.
    R. CUTHILL.

Chemiluminescence of solid sodium. R. M. BOWIE (J. Physical Chem., 1931, **35**, 2964—2967).—Moist air, O_2, H_2, or CO_2, but not the dried gases, produce light when in contact with solid Na. H_2O vapour, H_2S, dry HNO_3 vapour, and dry AcOH vapour also produce luminescence, but not SO_2 or the halogens. Liberation of H_2 always accompanied luminescence, which appears to be associated with the rupture of a H–O linking of a vaporised, polar mol. The spectrum consists of a narrow band with a max. at approx. 5100 Å.   L. S. THEOBALD.

Selective maxima in the spectral response curves of light-sensitive compounds as a function of valency. A. R. OLPIN (Physical Rev., 1930, [ii], **35**, 671).—Spectral response curves for photoelectric Na_2O_2, Na_2O, Na_3O, and Na_4O cells show all the selective maxima demanded by the Lindemann formula when n is chosen to agree with the valency of the metal. This condition is general for the other alkali metals, a max. response to red or infra-red light being dependent on the formation of a subvalent compound.   L. S. THEOBALD.

Temperature variation of the dielectric polarisation of benzene derivatives. E. BRETSCHER (Physikal. Z., 1931, **32**, 765—773).—The polarisations of $CH_2Ph\cdot OBz$ and of Et phthalate follow closely the $P=A+B/T$ law, their dipole moments being 2·69 and $2·08\times10^{-18}$, respectively. Pyrocatechol Et_2 ether follows the same law, but the val. of A varies widely

with the method of measurement adopted, differences being observed according to the solvent used and these differing from the val. of the mol. refraction. This is explained by assuming different states of the mol., with different electric moments.
    J. W. SMITH.

Dielectric constant of liquids under high pressure. W. E. DANFORTH, jun. (Physical Rev., 1931, [ii], **38**, 1224—1235).—Dielectric consts. were determined at two temp. and at pressures up to 12,000 atm. for PhCl, PhBr, eugenol, hexyl, *iso*butyl, and ethyl alcohol, glycerol, CS_2, C_5H_{12}, and Et_2O. Density is plotted against reciprocals of the Clausius–Mosotti function.   N. M. BLIGH.

Change of the dielectric constant of carbon disulphide with temperature. J. MAZUR (Nature, 1931, **128**, 761).—The dielectric const. of CS_2 increases from 2·630 at 20° to 2·936 at —90°, decreases to a min. of 2·810 at approx. —109°, and rises again to a max. of 2·819 at —112°.   L. S. THEOBALD.

Change of dielectric polarisation of nitrobenzene with temperature. M. WOLFKE and J. MAZUR (Nature, 1931, **128**, 584).—Computed vals. of the dielectric polarisation, P, of $PhNO_2$ fall linearly with temp. from 30° to 9·6°, where a sudden drop in the val. of P occurs, indicating that at 9·6° the mol. of $PhNO_2$ undergoes a change (cf. this vol., 899).
    L. S. THEOBALD.

Differences between the dipole moments of saturated and unsaturated substances. L. E. SUTTON (Proc. Roy. Soc., 1931, A, **133**, 668—695).—The dielectric const., refractive index, and density of C_6H_6 solutions of *o*- and *m*-nitrobenzonitrile, $CHPhCl_2$, $CPhCl_3$, and $CMeCl_3$ have been measured at 25°, from which the electric dipole moments have been calc. The available data supplemented by the above and a comparison of corresponding aliphatic and aromatic compounds show that there is an electron shift towards the C_6H_6 ring ($+$) when the group substituted is *o-p*-directing, and away from the ring ($-$) when it is *m*-directing. These effects occur independently of the polarisation caused by the group dipole and are in agreement with Lapworth's and with Robinson's theories of activation in conjugated systems. The mean effect is small, and probably there is a small effect in each mol., not a large effect in only a fraction of the mols. Similar effects occur in unsaturated open-chain compounds, and if the double linkings are conjugated these are greater than those in aromatic compounds.   L. L. BIRCUMSHAW.

Complex compounds of aluminium halides. H. ULICH and W. NESPITAL (Z. angew. Chem., 1931, **44**, 750—753).—Determinations of the mol. wt. and measurements of the dipole moment of additive compounds of the type $MHal_3,X$ and $MHal_2,2X$ lead to the assumption that these compounds have a tetrahedral configuration with the metal atom as centre. The compounds have large dipole moments which are approx. equal to the sum of the moments of the halide and the ligand.   A. R. POWELL.

Effect of thermal treatment on the electrical conductivity of cuprous oxide. F. WAIBEL (Wiss. Veröff. Siemens-Konz., 1931, **10**, No. 4, 65—69).—The

effect of thermal treatment on the conductivity of Cu_2O has been investigated from 0° to 1050° and at O_2 pressures of 0—1 atm. Prolonged tempering at 450—550° and rapid cooling lead to max. conductivity.
J. W. SMITH.

Rectifying action of cuprous oxide. F. WAIBEL (Wiss. Veröff. Siemens-Konz., 1931, **10**, No. 4, 70—72).—The rectifying action of pure Cu_2O in contact with foreign conductors is identical with that shown by the material formed on a Cu base.
J. W. SMITH.

Rectifying effect and photo-phenomena in carborundum crystals. B. CLAUS (Ann. Physik, 1931, [v], **11**, 331—356).—The rectifying influence of SiC crystals was studied in relation to the pressure of the contact metal. A yellow light and a blue light are emitted depending on the potential. The spectra of these emissions have been observed.
W. R. ANGUS.

Contact rectification. II. Cupric sulphide–magnesium junction. M. BERGSTEIN, J. F. RINKE, and C. M. GUTHEIL (Physical Rev., 1930, [ii], **35**, 1425).
L. S. THEOBALD.

Bismuth-black and its applications. A. H. PFUND (Physical Rev., 1930, [ii], **35**, 1434).—The optical properties and applications of black Bi films obtained by evaporating Bi from W wire in a vac. are described.
L. S. THEOBALD.

Optical rotation and atomic dimensions. Halogeno-tetra-acetyl derivatives of mannose, and their configurative peculiarities. D. H. BRAUNS (Bur. Stand. J. Res., 1931, **7**, 573—583; cf. A., 1929, 913).—The prep. of α-*iodomannose tetra-acetate*, m. p. 95°, $[\alpha]_D^{20}$ +190·5° in $CHCl_3$, is described. The vals. of $[\alpha]_D^{20}$ for the corresponding Cl and Br compounds are +90·13° and +131·57° (in $CHCl_3$). These vals. for $[\alpha]$ do not agree with the at. dimension relation established for the halogen derivatives of other monosaccharides (A., 1928, 157). This is due to the fact that in the derivatives of mannose, but not in the other halogen derivatives, the H of the first asymmetric C atom, to which the halogen is also attached, is influenced by atoms of the Ac group attached to the second C atom.
R. CUTHILL.

Refraction and dispersion of gaseous pentane and chloroform. H. LOWERY and T. S. HARTLEY (Proc. Physical Soc., 1931, **43**, 559—561).—*n*-Pentane has n_{Hg5461}, 1·001683, and $CHCl_3$ 1·001448 at n.t.p. conditions; Sellmeier formulæ are given for the range 4358—6708 Å.
A. B. D. CASSIE.

Refraction and dispersion of gaseous ethyl bromide. H. LOWERY and J. K. ELLIOT (Proc. Physical Soc., 1931, **43**, 562—563).—Gaseous EtBr has n_{Hg5461}, 1·001261 at n.t.p. conditions; a Sellmeier formula is given for the dispersion in the range 4358—6708 Å.
A. B. D. CASSIE.

Refractometric value of fluorine in organic compounds. G. SCHIEMANN [with R. PILLARSKY, S. KÜHNE, W. ROSELIUS, and W. WINKELMÜLLER] (Z. physikal. Chem., 1931, **156**, 397—418).—A detailed account of work already published (this vol., 1113).
H. F. GILLBE.

Optical properties of some aromatic organic crystals. K. L. NARASIMHAM (Indian J. Physics, 1931, **6**, 233—240).—The optical properties of Ph_2, phenanthrene, and fluorene have been studied. The birefringence for each is less than for $C_{10}H_8$. The results are discussed with respect to chemical constitution and X-ray crystal structure.
W. R. ANGUS.

Magnetic spectra produced by magnetic after-effects. V. ARKADIEV (Z. Physik, 1931, **72**, 116—124).—Theoretical, indicating the relationship for the fall in permeability of ferromagnetics in alternating fields found by various observers.
J. FARQUHARSON.

Magnetic and electric spectroscopy. V. ARKADIEV (Z. Physik, 1931, **72**, 125—129; cf. preceding abstract).—Theoretical.
J. FARQUHARSON.

Magnetic double refraction in aliphatic liquids. S. W. CHINCHALKAR (Indian J. Physics, 1931, **6**, 165—179).—The magnetic birefringence of many aliphatic liquids has been measured relative to $COMe_2$ as standard. A gradual diminution is found for ketones with higher alkyl groups. The val. for H_2O is smaller than for EtOH. Vals. for esters are of the same order as those for acids. The magnetic anisotropy is estimated for those mols. of which light-scattering data are available and is strongly positive for the CO group and negative for Me and OH. The negative birefringence of CS_2 is due to its strong optical anisotropy.
J. FARQUHARSON.

New type of magnetic birefringence. (SIR) C. V. RAMAN and S. W. CHINCHALKAR (Nature, 1931, **128**, 758—759).—Magnetic birefringence of the kind indicated by the orientation theory is shown by aq. solutions of Ce, Pr, Er, and Yt when observed in strong magnetic fields. With light in the visible region the birefringence is negative (same sign as shown by CS_2) and apparently proportional to concentration. Solutions of La and Gd show no such effect.
L. S. THEOBALD.

Electric double refraction in gases. J. W. BEAMS and E. C. STEVENSON (Physical Rev., 1930, [ii], **35**, 1440).—A new method for studying the Kerr effect in gases at high pressures and with intense electric fields indicates that the Kerr const. for CO_2 remains unchanged to within 2% between 15 and 45 atm. at 21°. A Kerr effect has been observed in O_2 and N_2 at 100 atm.
L. S. THEOBALD.

Physics of the nitrobenzene Kerr cell. II. Validity of Kerr's law for nitrobenzene in fields up to $1·5 \times 10^5$ volts per cm. F. HEHLGANS (Physikal. Z., 1931, **32**, 803—808; cf. this vol., 1220).—Kerr's law is valid within the range quoted.
A. B. D. CASSIE.

Objections to a proof of molecular asymmetry of optically active phenylaminoacetic acid. L. PAULING and R. G. DICKINSON (J. Amer. Chem. Soc., 1931, **53**, 3820—3823).—Polemical. The evidence presented by Clark and Yohe (A., 1929, 1294) is insufficient to prove mol. asymmetry or to fix the space-group.
J. G. A. GRIFFITHS.

Theory of space-groups in crystal structure determinations. M. L. HUGGINS (J. Amer. Chem.

Soc., 1931, **53**, 3823—3826).—Polemical. The space-groups assigned to several compounds (this vol., 290) are open to doubt.   J. G. A. GRIFFITHS.

Space-groups and molecular symmetry of optically active compounds : a reply. G. L. CLARK (J. Amer. Chem. Soc., 1931, **53**, 3826—3831 ; cf. preceding abstracts).—Further data are submitted, and the author, in general, maintains his position.
                    J. G. A. GRIFFITHS.

Why does molecular hydrogen reach equilibrium so slowly? H. HALL and J. R. OPPENHEIMER (Physical Rev., 1930, [ii], **35**, 132—133).—A mol. of para-H_2 may be converted by collision with any other mol. into ortho-H_2, or two mols. may be converted into ortho-H_2 by the interchange of nuclei between the mols. The probabilities of both processes are small. At n.t.p., para-H_2 should be half converted into ortho-H_2 in a period of the order of 10^8 sec.   L. S. THEOBALD.

Affinity. VIII. T. DE DONDER (Bull. Acad. roy. Belg., 1931, [v], **17**, 1001—1007).—Mathematical.
                    W. R. ANGUS.

Geometrical relations in the structures of the modifications of a substance. H. SHÔJI (Bull. Inst. Phys. Chem. Res. Tokyo, 1931, **10**, 909—930).—Structural changes in the space lattices of Fe, Co, Tl, Ce, Sn, C, NH_4Cl, NH_4Br, ZnS, CdS, AgI, TiO_2, $CaCO_3$, SiC, HgS, and SiO_2 as a result of their transformations have been studied, particularly in relation to at. and mol. cohesion. The following pairs of elements and compounds have similar structural relations between their individual modifications : Fe and NH_4Cl, Co and ZnS, Sn and TiO_2, C and $CaCO_3$.
                    E. S. HEDGES.

Internal structure of inorganic compounds at high temperatures. W. JANDER (Z. angew. Chem., 1931, **44**, 870—872).—The types of interchange of lattice positions which can occur in crystals are described. Methods available for the differentiation of these types include conductivity and diffusion measurements, and observations of reactivity between solids. Diffusion measurements with pairs of compounds of the type $M'_2M''X_4$, where M' is an alkali metal, M'' an alkaline-earth metal, and X a halogen, at 200—500°, show that the depth of penetration of the halogen of one compound into the other compound amounts often to about 0·6 mm., compared with 0·2 mm. or less for the metal. Complexes such as $(M''X_4)''$ can therefore exist only in very small concentration. Various spinels have been studied. The results show that $MgAl_2O_4$ and $ZnAl_2O_4$ are ionic conductors and that the mobility of the tervalent metals (Al, Cr) is greater than that of Mg or Zn.   H. F. GILLBE.

Three different effects of conjugation. A. F. RICHTER (Phil. Mag., 1931, [vii], **12**, 768—770).—Three types of conjugation are distinguished, according to the nature of the unsaturated group.
                    H. J. EMELÉUS.

Valency and symmetry. P. VINASSA (Atti R. Accad. Lincei, 1931, [vi], **13**, 642—645).—Theoretical.
                    H. F. GILLBE.

Valency electrons in the diamond. M. L. HUGGINS and R. PARRISH (Physical Rev., 1930, [ii], **35**, 136).—Small peaks midway between each two neighbouring C atoms on the density of scattering power curves may be due to electron pairs forming the valency linkings.   L. S. THEOBALD.

Nature of the chemical linking. II. The one-electron linking and three-electron linking. L. PAULING (J. Amer. Chem. Soc., 1931, **53**, 3225—3237 ; cf. this vol., 670).—Theoretical. A stable one-electron linking can be formed only when there are two conceivable electronic states of the system with essentially the same energy, the states differing in that for one there is an unpaired electron attached to one atom, and for the other the same unpaired electron is attached to the second atom. This criterion is satisfied in H_2^+, H_3^+, Li_2^+, and the boron hydrides. A three-electron linking, involving one eigen-function for each of 2 atoms and 3 electrons, can be formed when the two configurations A:·B and A·:B correspond with essentially the same energy, i.e., the energies of the two unperturbed configurations differ by less than the possible resonance energy. This criterion is satisfied in He_2, He_2^+, NO, N_2O, and O_2 which contains 2 3-electron linkings. The electronic configuration of metallic nitroso-complexes is discussed in relation to the magnetic moments.   J. G. A. GRIFFITHS.

Electron distribution in the chlorine ion. G. G. HARVEY and G. E. M. JAUNCEY (Physical Rev., 1930, [ii], **35**, 1427).   L. S. THEOBALD.

Aromatic electronics. H. H. HODGSON (Proc. Durham Phil. Soc., 1931, **8**, 313—322).—The electronic theory is applied to chromophores and auxochromes and to the decomp. of diazo-salts by aliphatic alcohols.
                    W. R. ANGUS.

Molecular energy levels and valency linkings. J. C. SLATER (Physical Rev., 1931, [ii], **38**, 1109—1144 ; cf. A., 1930, 126 ; this vol., 548).—The method of discussing the structure of atoms according to wave mechanics is extended to a consideration of electronic levels in mols.   N. M. BLIGH.

Molecular dissymmetry. R. DE MALLEMANN (Compt. rend., 1931, **193**, 651—654, 729—732).—Mathematical. An extension of the author's theories on optical rotatory power (cf. A., 1930, 981 ; this vol., 1215). The rotatory power of a fluid formed of the simplest possible mols. would in general be expressed by the sum of 576 ternary products.   C. A. SILBERRAD.

Inner molecular potential of substituents and its influence on the stability of *cis*- and *trans*-isomerides (dichloro-ethylene and -ethane). Stability of valency angles. H. A. STUART (Physikal. Z., 1931, **32**, 793—798).—Theoretical. Transverse vibration frequencies of simple linear mols. indicate great stability of the valency angle in $C_2H_2Cl_2$, temp. motions giving at most only a 10° deformation. The sphere of influence of the Cl atom is determined from the electrostatic energy of the dipole moment, polarisation, and dispersion effect, and explains the greater stability of the *cis*-form in $C_2H_2Cl_2$, and of the *trans*-form in $C_2H_4Cl_2$.   A. B. D. CASSIE.

Quantum theoretical analysis of the benzene problem. II. Quantum theory of induced polarity. E. HÜCKEL (Z. Physik, 1931, **72**, 310—337 ; cf. this vol., 1000).—The change in distribution of the mean electric density about the quasi-at. core of

the C_6H_6 ring is determined for mono-derivatives. The results are applied to substitution reactions of the mono-derivatives, and explain the difference in heat of activation of *o*- and *p*-mols., and its approx. equality for *m*- and the undisturbed ring. No simple vector addition of dipole moments is likely for di-substituted C_6H_6 rings.   A. B. D. CASSIE.

X-Ray analysis of the structure of hexachloro-benzene, using the Fourier method. (MRS.) K. LONSDALE (Proc. Roy. Soc., 1931, A, **133**, 536—552; cf. A., 1929, 750).—The unit cell is simple, monoclinic prismatic, with *a* 8·07, *b* 3·84, *c* 16·61 Å., β 116° 52′; *d* 2·044; 2 mols. per unit cell; space-group probably C_{2h}^5 ($P2_1/c$). From the {*h0l*} planes 80 reflexions have been observed and measured on the ionisation spectrometer. A Fourier analysis of the {*h0l*}} zone indicates that each C atom is roughly triangular, appearing to be definitely polarised in the direction of its appropriate Cl atom and of the two neighbouring C atoms. There is a kind of buffer region of low electron density outside each Cl atom. It is not possible to state whether the C_6H_6 ring in this compound is plane or not, but if it is plane, then the C–C distance must be 1·42 Å., the distance found in graphite and C_6Me_6.   L. L. BIRCUMSHAW.

Empirical crystal radii for ions with inert gas configuration. W. H. ZACHARIASEN (Z. Krist., 1931, **80**, 137—153).—The radii are determined for co-ordination no. 6, and a standard Coulomb force (that between a univalent cation and a univalent anion). They are deduced from the most trustworthy existing observations, cases of crystals containing anion contacts being avoided, K^+ (1·33 Å.) and Cl^- (1·81 Å.) being the bases. Corrections for different co-ordination nos., Coulomb forces (valency), and radius ratio are discussed and tabulated, and results compared with those of Goldschmidt and Pauling (cf. A., 1927, 399; 1929, 122, 747).   C. A. SILBERRAD.

Polar valency of phosphorus. T. MIŁOBĘDZKI (Rocz. Chem., 1931, **11**, 600—606).—Polemical.   R. TRUSZKOWSKI.

Natural classification of chemical compounds. I. F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1931, **1**, 359—366).—A certain parallelism exists between the curves obtained for various physical properties of compounds, arranged in series according to a classification based on their structure and on the at. nos. of their constituent atoms.   R. TRUSZKOWSKI.

Temperature variation of intrinsic magnetisation and associated properties of ferromagnetics. E. C. STONER (Phil. Mag., 1931, [vii], **12**, 737—763).—The observed characteristics of Ni are compared with those calc. for an idealised ferromagnetic.   H. J. EMELÉUS.

Magnetic properties of platinum: different varieties: influence of field: passage of one state to another. P. COLLET and G. FOËX (J. Phys. Radium, 1931, [vii], **2**, 290—308).—Four different specimens of Pt, at low temp. and under the same field conditions, gave moments of 8, 9·5, 11, and 13 magnetons, whereas at high temps. all give 8 magnetons. By increasing the field at low temp. the magneton val. is lowered. With fields below 3000 gauss Pt shows steps of const. paramagnetism with change in temp.   J. FARQUHARSON.

Dependence of the magnetic properties of nickel on elastic strain. M. KERSTEN (Z. Physik, 1931, **71**, 553—592).—The experimental initial permeability, magnetisation curves, and remanence of strained Ni wires are compared with theory.   J. FARQUHARSON.

Anomalous diamagnetism of bismuth. R. N. MATHUR and M. R. VARMA (Indian J. Physics, 1931, **6**, 181—182).—Bi sol and finely-powdered Bi are found to be much less diamagnetic than Bi metal crystals.   J. FARQUHARSON.

Diamagnetism and the colloidal state. S. R. RAO (Indian J. Physics, 1931, **6**, 241—254; cf. this vol., 1000).—With Bi and Sb free from oxides (cf. preceding abstract), χ decreases with particle size until it tends to a const. with diameters <0·5 μ. The val. for graphite falls rapidly with particle size. For Bi and C the fall in χ is proportional to the surface area of the particle. The decrease in χ with diameter is discussed by means of Richardson's electron theory (A., 1930, 1081).   J. FARQUHARSON.

Ferromagnetism and electrical properties. III. Relation between increase of resistance and magnetisation. K. SCHNEIDERHAN (Ann. Physik, 1931, [v], **11**, 385—405).—The increased resistance observed with a ferromagnetic material in a magnetic field is examined in relation to the magnetisation.   J. W. SMITH.

Influence of temperature on the diamagnetism of liquids. R. N. MATHUR (Indian J. Physics, 1931, **6**, 207—224).—The sp. susceptibility of H_2O increases with rise of temp. Aliphatic compounds show practically no change. Aromatic compounds, especially $PhNO_2$, show a definite decrease with rise in temp., which may be due to different degrees of mol. orientation at different temps.   J. FARQUHARSON.

Molecular aggregation. A. M. TAYLOR (Physical Rev., 1930, [ii], **35**, 668).—Van 't Hoff's equilibrium equation provides a method for determining mol. aggregation, and for I gives I_2 as the mol. size in the solid state in agreement with X-ray measurements.   L. S. THEOBALD.

Mol. size of crystalline carbon tetrabromide, determined by the partition coefficient method. J. P. SOHIER (Bull. Soc. chim. Belg., 1931, **40**, 403—426).—The m.-p. curve and the transition intervals for the system CCl_4–CBr_4 have been determined; the m.-p. and transition curves are continuous and are approx. parallel throughout the whole concentration range. The partition of CCl_4 between the saturated solution and the mixed crystals of CCl_4–CBr_4 has been investigated, and the mol. wts. of the components have been found to be the same in the two phases. Owing to the instability of CBr_4 at high temp., Barger's method was employed for the mol. wt. of the compound in solution; the mol. is $(CBr_4)_2$, in agreement with X-ray measurements with the form stable at low temp. The catalytic hydrogenation method of Ter Meulen and Heislinga is suitable for the analysis of mixtures of CCl_4 and CBr_4.   H. F. GILLBE.

Cohesion. J. E. LENNARD-JONES (Proc. Physical Soc., 1931, **43**, 461—482).—A lecture. Contributions of the new quantum mechanics to cohesion include density pictures of atoms permitting calculation of electrostatic interaction of atoms, exchange energies accounting for homopolar linking, pictures of asymmetrical atoms and their electron affinity, and finally an explanation of van der Waals forces as due to dynamic polarisation induced in atoms or mols. by mutual sympathetic motion of their charge densities.
A. B. D. CASSIE.

Energy of dissociation of normal Cd_2. J. G. WINANS and R. ROLLEFSON (Physical Rev., 1930, [ii], **35**, 1436).—The val. 1 volt for the dissociation energy of normal Cd_2 (A., 1929, 1352) is probably too high.
L. S. THEOBALD.

Decrease of the fundamental frequency as a preliminary stage in chemical decomposition. E. CREMER and M. PÓLÁNYI (Z. physikal. Chem., Bodenstein Festband, 1931, 770—774).—Theoretical. It is shown from the magnitude of the heat of activation of the dissociation of HI that a loosening of the intramol. forces plays a definite part in chemical change. This conclusion is supported by the decrease of the fundamental frequency observed in the Raman spectra of liquefying HCl and HBr. It is suggested that the effect results from homopolar influences in the sense of London's theory; agreement between observed and calc. data is unconvincing.
H. F. GILLBE.

Density and surface tension of isomerides of Δ^β-pentene and β-methyl-Δ^β-butene. W. F. SEYER (J. Amer. Chem. Soc., 1931, **53**, 2588—3596; cf. this vol., 579).—The data refer to temp. between $-70°$ and $80°$. The density and surface tension of the metastable pentene are between those of the other compounds. The surface energy of β-methyl-Δ^β-butene is approx. const., but that of the stable and especially that of the metastable pentene decrease with rise of temp. The parachor of the last two is 0·55 unit $>$ the calc. val., and decreases with rise of temp. The Eötvös const. is slightly higher than the normal val.
J. G. A. GRIFFITHS.

Hilger X-ray crystallograph and the cubic-crystal analyser. S. ZEIDENFELD (Proc. Physical Soc., 1931, **43**, 512—523).—Difficulties of ordinary powder crystal methods are enumerated, and the method of using slit, specimen, and photographic plate on the circumference of one circle is described; lines on the plate are cusps, and the time of exposure can be considerably reduced, increasing the val. of X-rays for commercial analysis. A. B. D. CASSIE.

X-Ray examination of electroplated chromium coatings. W. A. WOOD (Phil. Mag., 1931, [vii], **12**, 853—864).—The existence of hexagonal Cr, in addition to the normal body-centred cubic form, was confirmed, and conditions for obtaining it were determined. The broad diffuse X-ray diffraction lines from electrically deposited Cr were attributed to very finely-divided deposits, the grain size being estimated and correlated with the conditions of electro-deposition. H. J. EMELÉUS.

Crystal hydrate as a closed atomic and ionic microcosmos. M. A. RAKUSIN (Zentr. Min.,

Geol., 1931, **A**, 43—56; Chem. Zentr., 1931, i, 2577). A. A. ELDRIDGE.

Disappearance of the crystal in an isotropic active medium. L. ROYER (Bull. Soc. Franç. Min., 1930, **53**, 350—374; Chem. Zentr., 1931, i, 2839).—The effect of conc. aq. org. acids on calcite, dolomite, calamine, d- and l-tartaric acid, and S is discussed from the crystallographic point of view.
A. A. ELDRIDGE.

X-Ray determination of crystal orientation in silver sheet produced by cold rolling. C. B. HOLLABAUGH (Physical Rev., 1930, [ii], **35**, 1426).—The two symmetrical orientations produced in 99·9% sheet Ag by cold rolling are described.
L. S. THEOBALD.

Arrangement of the microcrystals in compressed single-crystal plates of aluminium. III. Y. FUKAMI (Mem. Coll. Sci. Kyoto, 1931, **A**, **14**, 97—113; cf. A., 1930, 139, 1098).—When a rectangular single-crystal plate of Al is compressed to 3—10% of its initial thickness the axis of the resulting fibrous arrangement of microcrystals is always parallel to the direction of flow of the metal on compression. The fibrous structure can be of four types. M. S. BURR.

Mechanical twins in white tin and zinc. K. TANAKA and K. KAMIO (Mem. Coll. Sci. Kyoto, 1931, **A**, **14**, 79—83).—The orientation of twin bands with reference to the mother crystal may be determined from the Laue photographs in the case of mechanical twins obtained by stretching the single crystal.
M. S. BURR.

X-Ray study of very pure iron. O. L. ROBERTS (Physical Rev., 1930, [ii], **35**, 1426).—Diffraction patterns of Fe, prepared from $Fe(NO_3)_3$ and spectroscopically free from C, show that the face-centred cubic structure exists at 921°. L. S. THEOBALD.

Radial asterism in multi-crystalline materials. C. NUSBAUM (Physical Rev., 1930, [ii], **35**, 1426).
L. S. THEOBALD.

Alkali hydrides. E. ZINTL, A. HARDER, and (in part) E. HUSEMANN (Z. physikal. Chem., 1931, **B**, **14**, 265—284).—Apparatus is described for preparing and analysing the alkali metal hydrides, and for introducing them into capillary tubes for crystal analysis by the powder method without exposure to the air. All have the NaCl structure and the following lattice consts. : LiH 4·084, NaH 4·880, KH 5·700, RbH 6·037, CsH 6·376 Å.; d calc., 0·77, 1·36, 1·43, 2·59, and 3·41, respectively. The effective hydride ion radii in these compounds are 1·26, 1·46, 1·52, 1·53, and 1·54 Å., respectively, in close agreement with previous work (A., 1929, 697). Intensity measurements do not support the view (A., 1925, ii, 296) that the hydride ions have free mobility in the lattice. The internuclear distances in LiH and NaH are about 30% greater than when these compounds are in the gaseous state, this result being in harmony with other work (A., 1929, 747). The similarity between the hydrides and the fluorides is discussed, and is shown by the fact that the lattice consts. of LiH and LiF differ by only 1·5%. These compounds do not, however, form an unbroken isomorphous series.
N. H. HARTSHORNE.

Asterisms in Laue photographs of rock-salt and internal tensions. V. LASCHKAREV and A. ALICHANIAN (Z. Krist., 1931, 80, 353).—The asterisms are no evidence of the existence of internal strains; they indicate only deformations of the crystal lattice.
C. A. SILBERRAD.

Structure of the azides from their electric dipole moments. L. E. SUTTON (Nature, 1931, 128, 639).—The electric dipole moments of Ph, p-chlorophenyl, and p-tolyl azides are 1·55, 0·35, and 1·96 × 10⁻¹⁸ e.s.u., respectively, and strongly support the ring structure. L. S. THEOBALD.

Crystal structure of potassium nitrate. D. A. EDWARDS (Z. Krist., 1931, 60, 154—163).—KNO_3 is orthorhombic holohedral; the unit cell has a 5·43, b 9·17, c 6·45 Å., with 4 mols.; space-group V_h^{16}. K has the co-ordination no. 9. C. A. SILBERRAD.

Gradual transition in sodium nitrate. II. Structure at various temperatures and its bearing on molecular rotation. F. C. KRAČEK, E. POSNJAK, and S. B. HENDRICKS (J. Amer. Chem. Soc., 1931, 53, 3339—3348; cf. this vol., 549).—X-Ray diffraction data for the powder between 25° and 290° show that at temp. >200° reflexions from planes in which O atoms alone contribute are progressively weakened until at 280°, where the gradual transition is complete, only uncertain traces remain. Otherwise, there is no major change in the structure within the transition interval. The phenomena are attributed to the initiation of rotation of the NO_3 ion about the trigonal axes of the crystal. The lattice consts. are : α 45° 35′, a 6·56 Å. at 280°; α 47° 14′, a 6·32 Å. at 25°. J. G. A. GRIFFITHS.

Crystal structure of potassium chromate. W. H. ZACHARIASEN and G. E. ZIEGLER (Z. Krist., 1931, 80, 164—173).—The unit cell has a 5·92, b 10·40, c 7·61 Å.; otherwise previous results are confirmed (cf. this vol., 1218). The structure is the same as that of the alkali sulphates (cf. A., 1929, 243; 1930, 671). C. A. SILBERRAD.

Crystal structures of silver and cuprous mercuri-iodides. J. A. A. KETELAAR (Z. Krist., 1931, 80, 190—203).—Ag_2HgI_4 at room temp. (cf. A., 1903, ii, 482) is pseudocubic tetragonal; a 6·340 Å., c/a 1·000±0·005. Cu_2HgI_4 is isomorphous; a 6·08, c 6·135. In both cases the unit cell contains 1 mol., and the space-group is V_d^1. The I atoms form an almost cubic close packing. C. A. SILBERRAD.

Habit-variation in crystals of potassium permanganate. H. E. BUCKLEY (Z. Krist., 1931, 80, 238—254; cf. this vol., 1115).—The effects of the following ions are considered (those of ions grouped together are similar) : (a) NO_3' (resembles ClO_3', Cr_2O_7'', and S_2O_6''); (b) PO_4''', AsO_4''', H_2AsO_4'; (c) H_2PO_4', CO_3''; (d) HPO_4'', $HAsO_4''$, MnO_4'; (e) B_4O_7'', BrO_3' (no effect). C. A. SILBERRAD.

Crystal structure of methyl orthosilicate. W. EULITZ (Z. Krist., 1931, 80, 204—237).—Me_4SiO_4 crystallises at −4° (approx.) in cubes, which pass into less stable anisotropic needles at a lower temp., although no definite transition point could be determined ; formation of the needles is favoured by rapid cooling. The isotropic form has a unit cell with

4 U

a 9·85 Å., and contains 4 mols. In each mol. the four C atoms are arranged tetrahedrally around the Si with the OMe groups directed away from the Si, an arrangement explaining the condensation to polymeric silicic esters (cf. A., 1930, 461). The 4 mols. are also arranged tetrahedrally *inter se*. The structure and interat. distances are closely similar to those of the inorg. silicates (cf. A., 1929, 749).
C. A. SILBERRAD.

Isomorphous relations and double salt formation between gypsum and brushite [ardealite]. F. HALLA (Z. Krist., 1931, 80, 349—352).—PO_3F'' and SO_4'' are isomorphous (cf. A., 1929, 662), as also F′ and OH′, hence PO_3OH'' and SO_4'' should be so. Powder diagrams of gypsum, brushite ($CaHPO_4,2H_2O$), and ardealite (the natural compound of the two) are closely similar, although that of the last named shows sufficient difference from that of an artificial mixture of its components to prove it to be a definite chemical individual (cf. dolomite). Its unit cell has a 10·47, b 14·64, c 6·28, and an analysis of a sample from the Cioclovina cavern (Siebenbürgen) gives CaO 31·61, P_2O_5 21·85, SO_3 21·25, H_2O 25·19, insol. in HCl 0·39, or approx. $CaSO_4,CaHPO_4,4H_2O$. As, however, $MgSO_4,7H_2O$ and $MgHPO_4,7H_2O$ are not isomorphous it is concluded that the isomorphous ions are $HPO_4'',2H_2O$ and $SO_4'',2H_2O$.
C. A. SILBERRAD.

[Crystal] structure of the trifluorides of aluminium, iron, cobalt, rhodium, and palladium. J. A. A. KETELAAR (Nature, 1931, 128, 303).—These trifluorides are all isomorphous and the hexagonal unit cell contains 3 mols.; AlF_3 a 4·93, c 6·25, FeF_3 a 5·20, c 6·66; CoF_3 a 5·06, c 6·63, RhF_3 a 4·88, c 6·81, and PdF_3 a 5·05, c 7·08 Å. These structures are not purely rhombohedral (cf. this vol., 549); they consist of alternating planes of metal and F ions, with the latter close-packed round the former. The distance between two F′ is slightly less than that calc. with a radius of 1·33; AlF_3 2·46, FeF_3 2·60, CoF_3 2·53, RhF_3 2·44, and PdF_3 2·52 Å. Other details are given.
L. S. THEOBALD.

Structure of cementite. S. SHIGETAKA (J. Fac. Eng. Tokyo, 1931, 20, 1—53).—Both Fe_3C and spiegeleisen have the simple orthorhombic lattice $Γ_0$ and the space-group V_h^{16}, the lattice consts. in each case being a 4·51, b 5·04, c 6·73 Å. In spiegeleisen the Fe atoms at the c_1 equiv. positions are replaced by Mn atoms. The C in austenite is present as free atoms, but when the transformation to martensite occurs the C atoms associate with neighbouring Fe atoms to form Fe_3C groups, ultimately segregating as Fe_3C crystals. C in metastable solution in α-Fe is present as Fe_3C groups. R. CUTHILL.

Gallium–zinc spinel. F. BUSCHENDORF (Z. physikal. Chem., 1931, B, 14, 297—302).—Ga_2ZnO_4, prepared by heating a mixture of Ga_2O_3 and ZnO at 1000°, is face-centred cubic, a 8·323 Å., n 1·74, $d_{calc.}$ 6·1544. The results show that Ga can replace Al in a Zn spinel without important alterations to the lattice. N. H. HARTSHORNE.

Crystal structure of eulytine. G. MENZER (Fortschr. Min. Kryst. Petr., 1931, 15, 67; Chem. Zentr., 1931, i, 2983).—The unit cell, a 10·272±0·003 Å.,

contains 4 mols. of $Bi_4Si_3O_{12}$. The lattice is body-centred cubic; space-group T_d^6.   A. A. ELDRIDGE.

Crystal cell of chlorites. C. MAUGUIN (Bull. Soc. Franç. Min., 1930, **53**, 279—300; Chem. Zentr., 1931, i, 2736).—The true chlorites have a rhombohedral unit cell, a 5·32, b 9·21, c 14 Å.
    A. A. ELDRIDGE.

Extent of noticeable cybotactic condition in a liquid as exhibited by triphenylmethane. G. W. STEWART (Physical Rev., 1930, [ii], **35**, 291).—X-Ray diffraction peaks for solid and liquid $CHPh_3$ indicate that the effective groupings of the mols. are of approx. the same extent in the finely-powdered crystal as in the liquid.   L. S. THEOBALD.

Diffraction of X-rays in organic mixtures. A. W. MEYER (Physical Rev., 1931, [ii], **38**, 1083—1093).—Diffraction curves are given for varying concentrations of the mixtures : EtOH–methyl*cyclo*hexane, BuOH–1 : 2-dimethyl*cyclo*hexane, quinoline–PhOH, paraldehyde–*cyclo*hexane, $C(NO_2)_4$–*cyclo*hexane, and $PhOH–H_2O$. Results indicate the existence in solution of a single type of cybotactic group, and in emulsions two types of cybotactic groups.   N. M. BLIGH.

Effect of impurities on the physical and crystallographic properties of hemimellitic acid. V. AGAFONOFF (Bull. Soc. Franç. Min., 1930, **53**, 25—34; Chem. Zentr., 1931, i, 2752).
    A. A. ELDRIDGE.

Crystal structure of wood. (FRL.) B. SCHMIDT (Z. Physik, 1931, **71**, 696—702).—An X-ray investigation of the alinement of cellulose crystals in different woods; in general, alinement is greater the more compact is the wood in an annual layer, and the greater is the alinement the greater is the tensile strength.   A. B. D. CASSIE.

X-Ray diffraction pattern of native cellulose. U. YOSHIDA and N. MATSUMOTO (Mem. Coll. Sci. Kyoto, 1931, A, **14**, 115—121).—The lattice form of native cellulose is tetragonal. $a=b=7·79$, c 10·26 Å.; there are 4 $C_6H_{10}O_5$ groups per unit cell.
    M. S. BURR.

Spontaneous crystallisation of supercooled melts and of supersaturated solutions. G. TAMMANN and H. E. VON GRONOW (Z. anorg. Chem., 1931, **200**, 57—73).—The theoretical relationship between the rate of formation of crystal nuclei in a liquid and the degree of supercooling (cf. A., 1929, 986) has been verified in the case of piperonal and of piperine. Measurements with saturated solutions of $K_2Cr_2O_7$ at various temps. show that with increasing supersaturation the time required for the formation of the first nucleus decreases. In general, with increasing supersaturation or supercooling the no. of nuclei formed in equal time intervals increases. Crystallisation centres cannot exist in a melt at temp. above the m. p.   O. J. WALKER.

Magnetostriction and hysteresis. W. N. BOND (Proc. Physical Soc., 1931, **43**, 569—571).—The longitudinal extension and intensity of magnetisation of unannealed wrought Fe both show hysteresis.
    A. B. D. CASSIE.

Magnetostriction in single crystals of iron and nickel. F. C. POWELL (Proc. Camb. Phil. Soc., 1931, **27**, 561—569).—A theoretical note.

Theory of magnetostriction. T. HAYASI (Z. Physik, 1931, **72**, 177—190).—Mathematical.
    A. B. D. CASSIE.

Cohesion. II. Effect of pressure and of percussion on rock-salt. H. TERTSCH (Z. Krist., 1931, **78**, 53—75).

Electric and mechanical effects in metal wires of heat, magnetic, and acoustic disturbance of structure. A. VON HIPPEL, O. STIERSTADT, and O. VON AUWERS (Z. Physik, 1931, **72**, 266—274; cf. this vol., 790).—Displacements of electric charge during magnetic and acoustic disturbances were investigated in relation to induced currents and the Barkhausen effect.   A. B. D. CASSIE.

Diminution of fissure hardness by adsorption of surface-active substances. Sclerometry and physics of dispersed systems. P. REHBINDER (Z. Physik, 1931, **72**, 191—205).—Diminution in hardness of a crystal surface on adsorption of polar substances from solution follows the adsorption isotherm, reaches a max. on saturation of the adsorption layer, and increases with the ease of orientation of adsorbed mols. The thermodynamics of the processes is discussed.   A. B. D. CASSIE.

Young's modulus determined with small stresses. D. K. FROMAN (Physical Rev., 1930, [ii], **35**, 120—121).   L. S. THEOBALD.

Superconductivity a polarisation phenomenon. J. C. MCLENNAN (Nature, 1931, **128**, 373).—No superconductivity discontinuity occurs in the resistance of Pb wires down to 2° abs. with frequencies as low as 12×10^6 per sec.   L. S. THEOBALD.

Electrical conductivity and structure of thin metal layers. II. Functional relations between specific resistance and layer thickness (refracting metal sublimates etc. at low temperatures). L. HAMBURGER (Ann. Physik, 1931, [v], **10**, 789—824).—The relation of electrical resistance of W and Ag to layer thickness is discussed, taking into account possible size of the elementary crystals, and the porous nature of the layer; noticeable conductivity first appears on formation of the disordered monat. layer.
    A. B. D. CASSIE.

Electrical resistance of carbon. Z. NISHIYAMA (Z. Physik, 1931, **71**, 600—615).—Pure graphite is a metallic conductor, and as a granular structure increases the electrical resistance increases and its temp. coeff. becomes negative.   A. B. D. CASSIE.

Electrical properties of spectroscopically pure zinc crystals. A. G. HOYEM (Physical Rev., 1931, [ii], **38**, 1357—1371).—The Voigt–Thomson symmetry relation was confirmed by measurement of the Thomson coeff. at 49·5° as a function of orientation. The thermal e.m.f. against Cu was determined as a function of orientation for the range —180° to 200°. The dependence of resistivity on temp. was investigated for the range —170° to 25°, and gave $4·058 \times 10^{-3}$ for the average temp. coeff. of resistivity. Corresponding data for Kahlbaum Zn were determined for comparison.   N. M. BLIGH.

Changes in the specific resistance of aluminium. G. E. DAVIS and G. GREENWOOD (Physical Rev., 1930, [ii], 35, 1429). L. S. THEOBALD.

Theory of the resistance of alloys. L. W. NORDHEIM (Physical Rev., 1930, [ii], 35, 1430). L. S. THEOBALD.

Thermocouples with elements of longitudinally and transversely magnetised ferromagnetic substances. S. SEASS (Physical Rev., 1931, [ii], 38, 1254—1257; cf. Ross, this vol., 1117).—The e.m.f. due to longitudinal and transverse magnetisation of the sections of a U-shaped conductor is investigated for different magnetic fields. Its relation to the Thomson and Ettingshausen–Nernst effect is discussed. N. M. BLIGH.

Transformation phenomena in so-called semi-conductors [group IV elements]. A. SCHULZE (Z. Metallk., 1931, 23, 261—264).—Measurements of the thermal expansion and electrical conductivity of pure single and polycryst. Si, Ge, and Ti failed to reveal evidence of allotropic modifications below 1000°, but Zr appears to undergo such a transformation at about 800—850°. A. R. POWELL.

Determination of thermal conductivity and its temperature-variation for medium conductors. C. R. ENSOR (Proc. Physical Soc., 1931, 43, 581—591).—A plate method for determination of thermal conductivity and its variation between 0° and 100° is described. A. B. D. CASSIE.

Measurement of the total heat of a liquid by the continuous mixture method. H. R. LANG (Proc. Physical Soc., 1931, 43, 572—580).—A development of Callendar's continuous mixture method (Phil. Trans., 1912, A, 212, 1) is discussed. A. B. D. CASSIE.

F. p. of organic compounds. XIII. Compounds containing from 7 to 10 carbon atoms. L. DEFFET (Bull. Soc. chim. Belg., 1931, 40, 385—402).—Data are given for the f. p., b. p., rate of change of b. p. with pressure, d_4^0, d_4^{15}, d_4^{30}, n at 7 wavelengths, and viscosity at 15° and 30° of a number of n-aliphatic halogen derivatives, alcohols, aldehydes, acids, nitriles, esters, acid chlorides and anhydrides, and amides of C_7, C_8, C_9, and C_{10} series. The regularity of the alternation of the f. p. in the various series is discussed. H. F. GILLBE.

M. p. of nitrobenzene and of benzene. I. MASSON (Nature, 1931, 128, 726).—Further determinations indicate that Richards' val. of 5·493° for the m. p. of C_6H_6 is approx. 0·1° too low and that the m. p. of dry $PhNO_2$ is near 5·83°. Mazur's val. of 5·5° (this vol., 899) is decidedly low. L. S. THEOBALD.

Inter-comparison of the high-temperature scale. W. E. FORSYTHE (Physical Rev., 1931, [ii], 38, 1247—1253).—Results for the scales in use at 9 leading laboratories in Europe and America are recorded, and show close agreement over the range 1400—2700° abs. N. M. BLIGH.

Method of measuring the temperature of gases. Application to the determination of their specific heats at high temperatures. M. CHOPIN (Ann. Physique, 1931, [x], 16, 101—149).—By measuring the fall in pressure produced on passing a gas through a narrow aperture the temp. of the gas can be calc. This method is applied to the measurement of the sp. heat of N_2 and CO_2 between 300° and 1000° for which the empirical equations $C_p=6·82+0·00058t$ and $C_p=8·9+0·62(t/100)^{0·03}$ are deduced, respectively. These are in good agreement with previous vals. J. W. SMITH.

[Thermal] emission from metals. W. DEL REGNO (Rend. Accad. Sci. Fis. Mat. Napoli, 1931, [iv], 1, 53—62).—The thermal emission of a number of metals has been studied at temp. between 50° and 500°. H. F. GILLBE.

Thermal expansion of lead. P. HIDNERT and W. T. SWEENEY (Physical Rev., 1930, [ii], 35, 296).—For 3 samples of cast Pb, the coeff. of linear expansion $\times 10^{-6}$ between 20° and 60°, 20° and 100°, 20° and 200°, and 20° and 300° varies from 28·3 to 29·2, 28·6 to 29·6, 29·4 to 31·2, and 30·9 to 32·5, respectively. L. S. THEOBALD.

Heats of fusion and molecular heats of aluminium halides. W. FISCHER (Z. anorg. Chem., 1931, 200, 332—342).—The heat capacities of $AlCl_3$, $AlBr_3$, and AlI_3 have been determined between —183° and 40° above the m. p. $AlCl_3$ has an abnormally small mol. heat just below its m. p., which latter is regarded as corresponding with a transformation into a form with lower m. p. The mol. heats of fusion are : $AlCl_3$ 8·5, $AlBr_3$ 2·7, AlI_3 3·8 kg.-cal. F. L. USHER.

Latent heat of fusion. K. HONDA and H. MASUMOTO (J. Study Met., Japan, 1930, 7, 65—71).—The increase in internal potential energy during melting was calc. For elements having a cubic lattice (1) the internal pressure at the m. p. is proportional to the square of the m. p. abs., (2) the increase in vol. of 1 g.-atom due to a rise of temp. of 1° at the m. p. is inversely proportional to the square of the m. p. abs., (3) the at. heat of fusion is proportional to the product of the vol. change of 1 g.-atom during melting and the square of the m. p. abs. CHEMICAL ABSTRACTS.

Calculation of the specific heats of solid organic compounds from Raman spectra. D. H. ANDREWS and J. C. SOUTHARD (Physical Rev., 1930, [ii], 35, 670—671).—Sp. heats calc. from Raman frequencies for MeOH, EtOH, C_6H_6, PhMe, PhCl, and PhBr over the range 15—260° abs. agree to within approx. 5% with the experimental vals. L. S. THEOBALD.

Cryoscopic constant, heat of fusion, and heat capacity of camphor. M. FRANDSEN (Bur. Stand. J. Res., 1931, 7, 477—483).—The latent heat of fusion of camphor at the m. p., 178·4°, is $10·74\pm0·40$ cal.$_{15}$ per g., from which the mol. lowering of the f. p. is calc. to be $37·7\pm1·4°$ mol.$^{-1}$ kg. The heat capacity of solid cryst. camphor over the range 20—178·4° is $0·4208+0·000215t\pm0·0035$ cal.$_{15}$ g.$^{-10}$ C.$^{-1}$, and that of liquid camphor over the range 178·4—210° is $0·571\pm0·045$ cal.$_{15}$ g.$^{-10}$ C.$^{-1}$ R. CUTHILL.

Specific heats of air, oxygen, and nitrogen from 20° to 370°. P. S. H. HENRY (Proc. Roy. Soc., 1931, A, 133, 492—506).—Improvements in the new flow method for comparing the sp. heats of gases (A., 1930, 282) are described; the method is accurate to

±0·5% at room temp. and 1·0% at higher temp. The vals. of C_v for air, O_2, and N_2 at 15° are in good agreement with the I.C.T. vals., but the rise in the temp. is much more rapid than that found by previous investigators (A., 1929, 128, 1372). The disadvantages of the sound-velocity method are discussed.   L. L. BIRCUMSHAW.

Specific heat of saturated vapours at the b. p. II. N. A. KOLOSOVSKI and V. V. UDOVENKO (J. Gen. Chem. Russ., 1931, 1, 255—262).—The mol. latent heat of vaporisation of liquids (L) and their sp. heat are given by $C_p - A - L_0/T + BT$, where A and B are consts. and T is temp. abs. The sp. heat of saturated vapour is given by $C_g = C_{pg} - L/T$, where C_{pg} is the sp. heat at const. pressure. The val. of C_g at the b. p. is negative for liquids the mols. of which contain < 10 atoms, and positive where > 10 atoms are present in the mol. The inversion temp., T_i, at which $C_g = 0$, is given by $T_i = -C_0/2\alpha \pm \sqrt{[(C_0/2\alpha)^2 + L/\alpha]}$.   R. TRUSZKOWSKI.

Deviations from the law of Neumann, Joule, and Kopp. III. Specific heat of mullite. N. A. KOLOSOVSKI (J. Gen. Chem. Russ., 1931, 1, 253—254). —Greater deviations from the above law are found for mullite than for cyanite, kaolinite, china clay, and bauxite.   R. TRUSZKOWSKI.

Thermal energy. I. Phenyl derivatives of methane, ethane, and related compounds. II. Phenyl derivatives of metals. R. H. SMITH and D. H. ANDREWS. **III. The octanols.** J. K. CLINE and D. H. ANDREWS. **IV. Comparison of continuous and discontinuous methods of measuring heat capacities. Heat capacities of aliphatic bromides.** R. F. DEESE, jun. **V. Heat capacity of nitrogen pentoxide at low temperatures.** J. McGRAW, jun. (J. Amer. Chem. Soc., 1931, 53, 3644—3660, 3661—3667, 3668—3673, 3673—3683, 3683—3693).—I. The technique has been improved (cf. A., 1930, 533) and heat capacities between 101° and 346° abs. are recorded for 25 Ph derivatives of CH_4, C_2H_6, C_2H_4, C_2H_2, MeOH, and MeCl. The heat capacity increment, at const. temp. in the hydrocarbon series, for the addition of a Ph group is almost const. Thus, the heat capacity of the Ph groups is independent of environment in these groups, the force const. of the C·C linking in C_2H_6 is not greatly affected by phenylation, and this linking is to be regarded as a structural unit relatively independent of environment.

II. Heat capacity data in the temp. range 101—346° abs. are recorded for $HgPh_2$, Hg di-p-tolyl, CPh_4, $SiPh_4$, $SnPh_4$, XPh_3, where X=N, P, As, Sb, Bi, and for Ph_2O, Ph_2S, Ph_2SO, and Ph_2SO_2. The heat capacity of the compounds XPh_3 generally increases with at. wt. of X, and substitution of C by Si produces a large increase. The results indicate a weakening of the force of linking between the Ph groups and the central atom as the wt. of the latter increases.

III. Data in the temp. range 101—311° abs. are recorded for 4 n- and 11 iso-octanols. Marked differences of heat capacity occur between 120° and 240° abs.; at other temp. the capacities are more nearly equal. The results are related to the internal energy and the tendency of the compounds to form glasses.

The heat capacity increases from straight-chain compounds which readily crystallise to unsymmetrical mols. which form glasses only.

IV. By means of a special calorimeter it is found that the continuous method, with a const. correction, affords accurate vals. of heat capacity. Data for Bu^aBr, m. p. 160·4° abs., n-amyl bromide, m. p. 185·1° abs., and n-hexyl bromide, m. p. 188° abs., between 93° and 248° abs. are recorded. n-Amyl bromide probably has a transition point at about 160° abs. The heats of fusion and the entropies at 298·1° are : Bu^aBr, 2208·6 g.-cal. per mol., 78·22 g.-cal. per 1°, n-amyl bromide 3435·3, 97·29, n-hexyl bromide 4318·2, 108·33.

V. The sp. heats of pyrex glass, NaCl, and N_2O_5 have been determined between 90° and 250° abs. by measuring the vol. of O_2 evolved when the heated sample is lowered into liquid O_2. The entropy of N_2O_5 between 0° and 250° abs. has been evaluated.   J. G. A. GRIFFITHS.

Heat capacity and entropy of silver iodate from 16° to 300° abs. Entropy of iodate ion. B. S. GREENSFELDER and W. M. LATIMER (J. Amer. Chem. Soc., 1931, 53, 3813—3817; cf. A., 1929, 142).—The heat capacities of $AgIO_3$ were determined between 16·16° and 297·6° abs., and the entropy at 298·1° abs. is computed to be 36·0 g.-cal. per 1°. The mol. heat and free energy of solution are 14,478 and 10,233 g.-cal. at 25°, from which the entropy of solution is 14·2 and that of the IO_3' ion in a $1M$ aq. solution is 34·3 g.-cal. per 1°.   J. G. A. GRIFFITHS.

Equations of state and thermodynamic functions for a substance with variable specific heat. W. P. BOYNTON (Physical Rev., 1930, [ii], 36, 787).— Theoretical.   L. S. THEOBALD.

New equation of state. H. J. BRENNEN (Physical Rev., 1930, [ii], 35, 129—130; cf. A., 1929, 252).— Dieterici's equation is criticised. The proposed new equation, $P(V-b) = RTe^{[-A(V-b)/RTV^n]}$, where n is the missing, third parameter, predicts that the law of corresponding states is true only for substances having the same val. of RT_c/P_cV_c.   L. S. THEOBALD.

Huang's general equations of energy and entropy of gases : the general adiabatic equation of gases. T. C. HUANG (Physical Rev., 1931, [ii], 38, 1385—1386; cf. this vol., 793).—Mathematical.   N. M. BLIGH.

Fusion and transition data for hydrocarbons. G. S. PARKS and H. M. HUFFMAN (Ind. Eng. Chem., 1931, 23, 1138—1139).—Heats of fusion, many of which have not hitherto been published, are tabulated for 59 hydrocarbons, including normal and branched paraffins, aliphatic olefines, aromatics, hydroaromatics, and naphthenes. Heats of transition are given for 8 cryst. hydrocarbons. There appears to be no quant. relation between heat of fusion and chemical constitution, but the following qual. tendencies are recognised : (a) in normal paraffins the mol. heats of fusion increase with increasing mol. wt., at first rapidly and later slowly; (b) the heat of fusion decreases markedly with increasing branching of a paraffin (with const. no. of C atoms); (c) cyclic hydrocarbons have lower heats of fusion than the corresponding normal paraffins; (d) withdrawal of H has no regular effect;

(e) when there are two cryst. forms of a given hydrocarbon at low temp., the sum of the heat of transition and the heat of fusion is comparable in magnitude with the heat of fusion of a compound existing in only one cryst. form. Thus, for cyclohexane this sum is 2230 g.-cal. per mol., as against 2350 g.-cal. per mol. for the heat of fusion of C_6H_6.

E. S. HEDGES.

Thermal data for organic compounds. X. Heat capacities, entropies, and free energies of hydrocarbons. H. M. HUFFMAN, G. S. PARKS, and M. BARMORE (J. Amer. Chem. Soc., 1931, 53, 3876—3888).—The following heats of fusion (g.-cal./g.) are recorded : propylene, 16·67; n-butane (I), 17·98; n-hexane, 36·14; n-octane, 43·21; n-nonane (II), 41·22; n-decane, 48·34; n-undecane (III), 34·12; n-dodecane, 51·33; methylcyclopentane, 19·55; 1 : 2-dimethylcyclopentane, 15·66; ψ-cumene, 25·15; isodurene (IV), 23·04; prehnitene, 20·0; p-cymene, 17·2; n-butylbenzene, 19·55; 2-methylnaphthalene, 20·11. The sp. heats of the above hydrocarbons and durene, pentamethylbenzene (V), anthracene, and phenanthrene have been measured over a wide range of temp. by the method previously described (A., 1925, ii, 491). (I), (III), and (V) exhibit solid transitions at 107°, 236·1°, and 296·8° abs.; the heats of transition are 8·7, 9·69, and 3·19 g.-cal./g., respectively. (II) and (IV) also exhibit solid transitions. The entropies of the hydrocarbons agree fairly well with those calc. (where possible) from the equation $S_{298} = 25·0 + 7·7n - 4·5r + 19·5p$ (cf. A., 1930, 677; this vol., 42). The free energies of 14 of the above hydrocarbons show that the order of decreasing thermodynamic stability at 298° abs. is paraffin, cycloparaffin, olefine, aromatic hydrocarbons. H. BURTON.

Adiabatic expansion of water and viscous liquids. G. TAMMANN and A. ELBRÄCHTER (Z. anorg. Chem., 1931, 200, 153—167).—When H_2O expands adiabatically under pressures of 1600 kg. per sq. cm. and upwards at 0° or at 30° the observed fall in temp. is less, and below 600 kg. and at 0° it is greater, than is calc. on the assumption that internal equilibrium is established instantaneously. At 70° there is no divergence at any part of the pressure range. The work of expansion of glycerol, aq. sucrose, and aq. $ZnCl_2$ is equal to the heat effect if the abs. viscosity is less than about 0·6, whereas at higher viscosities an increasing proportion of the work remains in the liquid as potential energy.

R. CUTHILL.

Definition and evaluation of the fugacity of an element or compound in the gaseous state. G. TUNELL (J. Physical Chem., 1931, 35, 2885—2913).—Mathematical. The definition of fugacity adopted is based on the physical hypothesis stated by Lewis and Randall that $\lim_{P=0}(RT'/P - v) = K(T')$, where $K(T')$ denotes at a given temp. a const. difference from zero except at the Boyle temp. The equation of definition leads directly to the equations given by Lewis and Randall as their definition of fugacity. The α function of gaseous N_2, calc. from the Beattie–Bridgeman equation, is represented graphically, and the calc. vals. of α are compared with experimental vals. obtained by other investigators. The fugacity

equation for gaseous N_2, with numerical coeffs. based on the consts. of Beattie and Bridgeman, is given.

L. S. THEOBALD.

Cubic compressibility of certain substances. L. H. ADAMS and R. E. GIBSON (J. Wash. Acad. Sci., 1931, 21, 381—390).—The compressibilities of pyrex glass, vitreous SiO_2, obsidian, duralumin, NH_4NO_3, K_2SO_4, Na_2SO_4, and Bu^a_2O have been measured.

N. H. HARTSHORNE.

Isothermal and adiabatic compressibilities, specific heat, and heat conductivity of liquids. H. SHIBA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 16, 205—241).—Complete data, together with those of previous investigators, and calc. vals. are tabulated for the following liquids : CS_2, $CHCl_3$, CCl_4, $MeNO_2$, C_6H_6, PhCl, PhBr, $PhNO_2$, PhMe, m-xylene, n-hexane, $COMe_2$, MeOH, EtOH, PrOH, BuOH, amyl alcohol, allyl alcohol, ethylene glycol, Me, Et, Pr, Bu, amyl, and octyl acetates, Et propionate and butyrate.

N. M. BLIGH.

Dependence of viscosity in liquids on the molecular space arrangement as shown by X-ray diffraction. R. L. EDWARDS and G. W. STEWART (Physical Rev., 1930, [ii], 35, 291).—A comparison of X-ray and viscosity measurements for 21 octyl alcohols shows that when the OH group is in a fixed position and the Me group is placed in possible positions in the mol. the change in viscosity coeff. varies in a manner similar to that of the magnitude of the secondary diffraction peaks. L. S. THEOBALD.

Viscosity of liquids. G. W. STEWART (Nature, 1931, 128, 727).—Andrade's theory of viscosity is, in a limited way, in harmony with the cybotactic condition of liquids revealed by X-ray diffraction.

L. S. THEOBALD.

Azeotropism. New equations of indifferent states. I. R. DEFAY (Bull. Acad. roy. Belg., 1931, [v], 17, 940—955).—The theory of indifferent states is developed in a simpler manner than previously and the equations of these states are presented in a simpler form. The theory is applicable also to systems not in equilibrium. J. W. SMITH.

Azeotropism. New equations of indifferent states. II. R. DEFAY (Bull. Acad. roy. Belg., 1931, [v], 17, 1066—1094; cf. preceding abstract).—The idea of indifferent states is extended to systems not in equilibrium and new equations are given.

W. R. ANGUS.

Dynamic azeotropism. VII. (MLLE.) G. SCHOULS (Bull. Acad. roy. Belg., 1931, [v], 17, 927—939).—Mathematical. J. W. SMITH.

Isomorphous replaceability of atoms and atom groups bound by non-polar linkings. H. G. GRIMM, M. GÜNTHER, and N. TITTUS (Z. physikal. Chem., 1931, B, 14, 169—218).—Atoms and groups which are similar according to the hydride displacement principle (A., 1925, ii, 1123) may be expected to replace one another in solid compounds without causing much alteration in the cryst. structure. Examination of 89 such org. binary systems, many of which have not been previously investigated, shows, however, that mixed crystals are formed in about half of them only. N. H. HARTSHORNE.

Influence of temperature on the diffusion coefficient of solid metals. O. MATANO (Mem. Coll. Sci. Kyoto, 1931, A, **14**, 123—130; cf. A., 1930, 1509; this vol., 1118).—By the electrical resistance method for determining the coeff. of diffusion D at different temp. it has been confirmed that the relations $D = Ae^{-a/\theta}$ and $D = A0e^{-a/\theta}$, where A and α are consts. and θ is the abs. temp., represent the experimental results for the Ag–Au and Ni–Cu systems between 300° (or 330°) and 500°.

M. S. BURR.

Zinc–manganese alloys. N. PARRAVANO and V. MONTORO (Mem. R. Accad. Ital., Sci. Fis. Mat. Nat., 1930, **1**, Chim., No. 4, 15 pp.; Chem. Zentr., 1931, i, 2801).—X-Ray examination shows the presence of three phases : η (hexagonal Zn lattice, up to 0·98% Mn), ε (hexagonal Zn lattice; 2 $MnZn_7$ in the unit cell), and γ (space-centred cubic lattice; 12 $MnZn_3$ in the unit cell). A. A. ELDRIDGE.

X-Ray investigation of some copper–aluminium alloys. G. D. PRESTON (Phil. Mag., 1931, [vii], **12**, 980—993).—The cubic γ phase exists from 31 to 35·5 at.-% Al. It is followed by a hexagonal phase with approx. 43 at.-% Al, and then by an orthorhombic phase, CuAl (a 4·087±0·005, b 12·00±0·02, c 8·635±0·01 Å., 16 mols. CuAl in unit cell). The hexagonal phase is probably stable down to room temp. : the orthorhombic phase exists at 600°, but probably undergoes transformation on cooling.

H. J. EMELÉUS.

X-Ray fibre structure of alloys containing precipitated crystals. C. S. BARRETT (Physical Rev., 1930, [ii], **35**, 1425).—A discussion.

L. S. THEOBALD.

Diagram of state of copper–gold alloys. G. GRUBE, G. SCHÖNMANN, F. VAUPEL, and W. WEBER (Z. anorg. Chem., 1931, **201**, 41—74).—Previous work is supplemented by micrographic examination and by measurements of electrical conductivity and thermal expansion. Between 17 and 85 at.-% Au the primarily formed α mixed crystals are transformed below 460° into three new series of mixed crystals, viz., β with Cu_3Au as principal constituent, γ with CuAu, and δ (> 65 at.-% Au) which is free from Cu_3Au. These series are separated by narrow regions (34—38, 62—64·5%) of heterogeneity. The mode of transformation of the cubic mixed crystals into the tetragonal CuAu is discussed.

F. L. USHER.

Equilibrium diagram of the tin–antimony system and the crystal structure of the β-solid solution. K. IWASÉ, N. AOKI, and A. ÔSAWA (Sci. Rep. Tôhoku, 1931, **20**, 353—368).—The equilibrium diagram has been determined by thermal and X-ray analyses, by resistivity measurements, and by micrographic examination. The results in general confirm the work of earlier workers. The change which occurs at 320° with 30—70% Sb is, however, attributed to an allotropic transformation in the β solid solution; below 320° this phase has a simple cubic structure.

A. R. POWELL.

System silver–copper–manganese. M. KEINERT (Z. physikal. Chem., 1931, **156**, 291—303).—The behaviour of this system has been investigated microscopically, and a triangular diagram is constructed on the basis of 18 points. Alloys with < 30% Mn yield a homogeneous liquid phase; those with between 30 and 90% may give rise to 2 liquid phases, the saturation curve of which has been approx. determined. The solid phases consist of Ag crystals containing small amounts of the other metals, and of Cu–Mn mixed crystals containing < 7% Ag. The hardness of alloys with > 80% Ag is greatly influenced by suitable thermal treatment.

F. L. USHER.

Crystal structures of certain chromium–nickel alloys. F. C. BLAKE and J. O. LORD (Physical Rev., 1930, [ii], **35**, 660).—Ni–Cr alloys containing 63—85% Cr show the following phases : (i) body-centred Cr, d 6·93, (ii) Cr_2Ni, with 96 atoms per unit cell which consists of 4 interpenetrating lattices of Cr, and body-centred tetragonal lattice with a 10·64 Å. and axial ratio 1·040; (iii) Cr nitride, close-packed hexagonal with a 2·751 Å. and axial ratio 1·605; unit cell, 2 atoms of Cr and 2 of Ni; $d_{calc.}$ 7·75; space-group D_3^4. L. S. THEOBALD.

Magnetic structural analysis. I. N. S. AKULOV (Z. Physik, 1931, **71**, 764—777).—It is shown that the position of the points of max. curvature on the magnetisation curve of a pseudo-isotropic alloy depends chiefly on the lattice structure of the elementary crystal. By deformation of the alloy, the anisotropic point can be moved. These points make it possible to study the crystal structure by magnetic methods. A. J. MEE.

Microstructure of some magnetic alloys of high platinum concentration. F. W. CONSTANT (Physical Rev., 1930, [ii], **35**, 116).—Alloys containing 5 and 10% Co are solid solutions; no evidence of eutectic structure is obtained. Cubic formations are shown by many of the crystals.

L. S. THEOBALD.

Micro-optical investigation of non-ferrous alloys by polarised light. M. VON SCHWARZ (Metallurgia, 1931, **4**, 180—186).—The microstructure of a number of materials, notably Cu–Si alloys, has been investigated. Photomicrographs resulting from the use of crossed Nicols appear sharp in colour contrast, but are sometimes indefinite in outline as compared with those obtained under ordinary methods of lighting or with parallel Nicols. The method serves to differentiate between constituents similar in colour under ordinary methods of illumination, but differing in mode of crystallisation and optical behaviour. Thus Cu_2O, being anisotropic, appears blue under parallel Nicols and red under crossed Nicols, whereas the isotropic silicon-copper appears blue in all positions of the prisms.

E. H. BUCKNALL.

Physical properties of concentrated aqueous salt solutions. J. N. PEARCE and M. A. HOOPER (Proc. Iowa Acad. Sci., 1930, **37**, 225).—Vals. of d^{25} and n^{25} and dielectric const. for alkali halides were determined from $0·1M$ nearly to saturation.

CHEMICAL ABSTRACTS.

Diffusion of liquids. E. MÜNTER (Ann. Physik, 1931, [v], **11**, 558—578).—A photographic method is used for the determination of concentration gradients.

Diffusion measurements with three pairs of substances agree with those obtained by other methods. The optical method has the advantage that observations can be made over the complete concentration range, and over short time intervals. A. J. MEE.

Changes of state in viscous systems. I—VI. E. BERL and collaborators (Kolloidchem. Beih., 1931, 34, 1—79).—Partly a summary of work published during the last 10 years (cf. A., 1930, 1114; this vol., 301, 302) on the dependence of the viscosity of complex systems on concentration and temp. The viscosity and dielectric const. of "voltol" oils have been measured. The slight deviation of these liquids (also H_2O and HCO_2H) from the linear relation between n and $1/T$ is correlated with a high dipole moment. The results suggest that the "voltol" oils consist of associated radicals, which are dissociable in solution, and mol. wt. determinations support this view. An electrodynamic theory of viscosity, applicable to systems in all states of aggregation, is developed and shown to be consistent with the results.
E. S. HEDGES.

Ternary systems : water, isopropyl alcohol, and salts at 25°. P. M. GINNINGS and Z. T. CHEN (J. Amer. Chem. Soc., 1931, 53, 3765—3769; cf. A., 1930, 989).—The miscibility of $Pr^\beta OH$ and H_2O has been examined in the presence of inorg. salts. $Pr^\beta OH$ is salted out more easily than EtOH or MeOH, but less easily than $Pr^\alpha OH$ or tert.-butyl alcohol. K_2CO_3 and KF have the greatest salting-out effects.
J. G. A. GRIFFITHS.

Ebullioscopic method applied to ternary heteroazeotropic mixtures : ternary heteroazeotropic mixture of carbon disulphide, acetone, and water. W. SWIENTOSLAWSKI and (MLLE.) L. WAJCEN-BLIT (Compt. rend., 1931, 193, 488—489, 664—666).—The author's method (cf. this vol., 704) is applied to a mixture of CS_2, $COMe_2$, and H_2O, for which the heteroazeotropic b. p. is 38·042°, and composition (by wt.) CS_2 75·21, $COMe_2$ 23·98, H_2O 0·81%.
C. A. SILBERRAD.

Solubility of gases. I. Solubility of argon at high pressures. B. SISSKIND and I. KASARNOV-SKI (Z. anorg. Chem., 1931, 200, 279—286).—The solubility of A in H_2O (0·2°, 25—125 atm.), MeOH and EtOH (0·2°, 25—100 atm.), and in n-pentane, Et_2O, $COMe_2$, and PhCHO (0·2°, 25 atm.) has been determined. It diminishes in the order EtOH, MeOH, H_2O, and exhibits large deviations from Henry's law, which are negative for H_2O and positive for the alcohols. The significance of the results is discussed.
H. F. GILLBE.

Solubility of salts in liquid ammonia. P. C. SCHERER, jun. (J. Amer. Chem. Soc., 1931, 53, 3694—3697).—The data refer to NH_4Cl, NH_4Br, NH_4I, and NH_4NO_3, and the corresponding Na salts between −31° and −51°. The solubility increases with rise of temp. except in the case of $NaNO_3$, for which compound formation with the solvent is indicated.
J. G. A. GRIFFITHS.

Solubility of copper iodate in aqueous salt solutions. B. H. PETERSON and E. L. MEYERS (Proc. Iowa Acad. Sci., 1930, 37, 223—224).—The solubility of $Cu(IO_3)_2$ in H_2O and in solutions of KCl, K_2SO_4,

$MgCl_2$, and $MgSO_4$ has been measured. Below 0·007M the observed activity coeffs. agree with those calc. from the Brönsted and Le Mer form of the Debye–Hückel equation. CHEMICAL ABSTRACTS.

Solubility of sodium chloride in acetic acid. O. WILLE (Fischwirt., 1931, 7, 37—39; Chem. Zentr., 1931, i, 3444—3445).—The saturated solutions contain 27·6, 28·2, 28·5, 29·0, 29·3, 29·7, 30·1, 30·6, 31·2, 31·9, 32·0% NaCl when the AcOH is present to the extent of 8·4, 7·6, 6·9, 6·1, 5·4, 4·4, 3·5, 2·6, 1·9, 0·9, and 0%, respectively. A. A. ELDRIDGE.

Comparison of solubilities of calcium and strontium p-bromobenzoates in acetone–water mixtures. J. C. BAILAR (Ind. Eng. Chem. [Anal.], 1931, 3, 362—363).—The solubilities of the p-chloro-, p-bromo-, and p-iodo-benzoates of Ca, Sr, and Ba in 94% $COMe_2$ have been determined. Ca p-bromobenzoate has a solubility about 45 times as great as that of the Sr salt. Attempts to effect a quant. separation of Ca and Sr, using these salts, failed.
E. S. HEDGES.

Equilibrium in the system phthalic acid–potassium phthalate–water. S. B. SMITH (J. Amer. Chem. Soc., 1931, 53, 3711—3718).—Solubility data have been determined at 0°, 25°, 35°, and 60°; the double salt $K_2C_8H_4O_4,4C_8H_6O_4,4H_2O$ is stable in contact with saturated solutions below 36·67°, $KHC_8H_4O_4$ should be recrystallised from aq. solution above 35° (cf. A., 1920, ii, 628).
J. G. A. GRIFFITHS.

Adsorption of certain vapours by activated charcoal. J. N. PEARCE and P. E. PETERS (Proc. Iowa Acad. Sci., 1930, 37, 223).—Isotherms (almost rectilinear for the hydrocarbons) for the adsorption of C_2H_6, C_3H_8, Me_2O, and Et_2O by activated charcoal have been obtained at 0—183° and 1—760 mm. At low temp. the isotherms for the hydrocarbons show a peculiar inflexion. The amount of vapour adsorbed decreases with increase in the complexity of the adsorbed mols. CHEMICAL ABSTRACTS.

Sorption of hydrogen on copper. I. Adsorption and the heat of adsorption. II. Rate of dissolution. A. F. H. WARD (Proc. Roy. Soc., 1931, A, 133, 506—522, 522—535).—I. The sorption and heats of adsorption of H_2 on activated Cu have been measured for successive additions of gas at 25° and 0·001—3·0 cm. Differences in the velocity of surface adsorption and solid solution formation permit the separation of these processes and the determination of the true adsorption isotherms. These are reversible. The heats of adsorption (corr. for gas dissolved and the heat of compression of the gas) are independent of the amount of gas adsorbed, but decrease after each baking of the metal until a val. of 9000 g.-cal. per mol. is reached. The isotherms are unaffected by heating below 150°, the temp. of prep. of the metal, but above this temp. the adsorption decreases.

II. The adsorption of H_2 on Cu and rates of diffusion into the metal have been measured between 25° and 200° for various pressures of gas. As the rate of diffusion at any temp. is proportional to the amount of gas adsorbed on the surface, this rate is related to the gas pressure by the same form of equation as the adsorption isotherm. From the variation of rate of

diffusion with temp. the energy of activation of the process is calc. to be 14,100 g.-cal. per mol. It is considered that grain-boundary diffusion occurs rather than lattice diffusion, and the previously accepted theory that the diffusing mols. are dissociated into atoms is criticised.   L. L. BIRCUMSHAW.

Adsorption and activation of carbon monoxide at palladium surfaces. [Hydrogenations.] H. S. TAYLOR and P. V. MCKINNEY (J. Amer. Chem. Soc., 1931, **53**, 3604—3624).—$PhNO_2$ is reduced quantitatively to NH_2Ph at room temp. by H_2 and Pd-black freshly reduced from PdO. Alcohols and rise of temp. accelerate the reaction, which is retarded by H_2O and NH_2Ph and almost completely inhibited by C_6H_6. The temp. of dehydrogenation of PhEt vapour is lowered by Pd-black and Pd–asbestos and the yield of styrene is increased by adding air. A $1CO : 5H_2$ mixture affords a 90% yield of CH_4 in contact with Pd-black at 300°. CO strongly inhibits the reduction of PdO by H_2. Pd does not catalyse the reaction $2CO=C+CO_2$.

Adsorption isotherms for CO on Pd at temp. between 86° and 553° abs. are given. More gas is adsorbed at 86° abs. than at 195° abs.; the gas is more easily desorbed at 86°. The adsorption at 273° abs. is greater but slower than at 86° abs. The isobars for pressures >10 mm. have high vals. at 86°, decreasing to min. at 195°, rising to max. at 273°, followed by decreases with further rise of temp. These data and the effect of change of temp. on the rate and magnitude of adsorption support the view that chiefly " physical " or " low-temp." adsorption occurs at 86° and 195°, whilst adsorption requiring energy of activation has a max. at 273° on unsintered and at 383° on sintered Pd. The heat of activated adsorption is approx. 15,000 g.-cal. per mol. on the less active parts of the surface.
                          J. G. A. GRIFFITHS.

Adsorption of aliphatic acids on evacuated charcoal. L. K. LEPIN (J. Gen. Chem. Russ., 1931, **1**, 388—392).—The adsorptive power of degassed charcoal for aliphatic acids from C_1 to C_4 is less than that of ordinary charcoal, whilst for acids above C_4 no difference is observed. These effects are explained on the assumption that the surface of degassed and ordinary charcoal is covered with a layer of a less and a more basic oxide, respectively. For the acids C_1–C_4 adsorption corresponds with the displacement of oxide by the CO_2H group, which is oriented towards the charcoal surface, but with the higher acids the orientation is reversed, the terminal Me group being in contact with the adsorbent surface.
                          R. TRUSZKOWSKI.

Influence of surface layers of adsorbed gas on the optical constants of mercury. (FRL.) E. HERSCHKOVITSCH (Ann. Physik, 1931, [v], **10**, 993—1016).—The influence on the optical consts. of Hg of adsorbed layers of air, H_2, O_2, CO_2, Ne, N_2 and C_2H_2 has been examined. The mol. thickness of the layers cannot be estimated.   W. R. ANGUS.

Adsorption at the surface of a solution W. F. K. WYNNE-JONES (Phil. Mag., 1931, [vii], **12**, 907—912; cf. A., 1925, [ii], 960).—The total amount of EtOH adsorbed at the surface of aq. EtOH suggests the formation of a unimol. surface layer of EtOH mols.

at concentrations >30% EtOH. Similar results are obtained for aq. solutions of MeOH and $COMe_2$.
                          H. J. EMELÉUS.

Aminolysis of alanine. E. BAUR (Z. physikal. Chem., Bodenstein Festband, 1931, 162—171).—The decomp. of alanine solutions in presence of animal C at 100° is incomplete, but a condition of true equilibrium is not attained. The concentration of NH_4 lactate formed is proportional to the wt. of C per litre, and it appears that the primary decomp. is that of an adsorption compound of alanine and C and that the lactate formed is present initially as a second adsorption compound. The reaction ceases when the active points capable of adsorbing the lactate are fully occupied. Other reaction products are $(NH_4)_2CO_3$, HCO_2NH_4, EtOH, and EtCHO, and the mechanism of their formation is discussed. The heat effect of the aminolysis is —7·8 kg.-cal.   H. F. GILLBE.

Starch–iodine reaction. J. FIELD (J. Biol. Chem., 1931, **92**, 413—419).—Radiomicrometric titration shows that aq. solutions of maize and wheat starches have, at the same concentration, approx. the same I capacity. This capacity is not proportional to the starch concentration, but is influenced by a dilution factor in a way which supports the view that " starch iodide " is an adsorption compound.
                          A. COHEN.

Surface-tension determination by the ring method, and the surface tension of dilute solutions of salts. G. SCHWENKER (Ann. Physik, 1931, [v], **11**, 525—557).—The ring method has been considerably improved so that it is now possible to carry out a determination with an accuracy of 0·022%. Relative measurements can be made with an even greater accuracy. The surface tension of H_2O is 75·59 dynes per cm. at 0° and 72·86 at 18°. The surface tensions of aq. solutions of LiCl, KCl, and NaCl in the concentration range 0—0·15N have the same val.   A. J. MEE.

Surface tension of different dilutions of Boys' soap solution. L. D. MAHAJAN (Phil. Mag., 1931, [vii], **12**, 954—959).—The surface tension of H_2O, measured by the drop-wt. method or surface-tension balance, falls rapidly on adding up to 5% of soap solution, passes through a min. at approx. 30 dynes per cm. (15% soap solution), and rises very slowly with further additions.   H. J. EMELÉUS.

Method for study of the unimolecular film. E. GORTER and W. A. SEEDER (Naturwiss., 1931, **19**, 738).—Stationary waves are generated on a H_2O surface by an electrically-driven tuning fork, and the reflected light is brought by means of a lens to a focus. As the result of the wave movement the point of light moves in a straight line. A film of the compound under investigation is produced on the surface of the liquid, e.g., by allowing a solution in light petroleum to evaporate, and the damping which this causes results in a shortening of the straight line. This effect affords a new method for the study of surface films.   W. O. KERMACK.

Membrane behaviour. I. Equilibrium conditions with gelatin membranes in acetate buffer solutions. W. L. FRANCIS (Proc. Roy. Soc., 1931,

A, **133**, 587—604).—Equilibrium potentials across membranes of unglazed Berlin porcelain (with and without gelatin) have been measured for buffer concentration gradients of 10 : 1, using $N/40$—$N/400$ and N—$0.1N$ solutions. The results for the p_H range 2.35—7.3 support the modified diffusion theory which attributes the potential to altered ionic mobilities within the membrane, but more direct evidence, obtained from determinations of the transport nos. of the Na˙ and OAc′ ions across the membrane in $0.5N$ solution, is not in agreement with this theory. The transport no. of the OAc ion remains steady over the p_H range 0.29—0.37. A theory offered to explain the results is based on the known behaviour of gelatin in electrolyte solutions.

L. L. BIRCUMSHAW.

Determination of osmotic pressure by isothermal distillation. I. M. ULMANN (Z. physikal. Chem., 1931, **156**, 419—434).—Various modifications of the high-vac. apparatus of Frazer and Patrick are described. The apparatus may be freed from air within 5—6 hr. Troublesome distillation of the solvent has been obviated, and the observations have been rendered independent of temp. fluctuations. Typical measurements with $0.01M$ solutions of dextrose, sucrose, and raffinose are described.

H. F. GILLBE.

Striations in chemical processes. IV. D-**Striations and related phenomena.** E. SCHALLY (Monatsh., 1931, **58**, 399—427).—By examining the shadow distribution of the D-striations (cf. A., 1930, 149) when one solution is allowed to flow into another of the same refractive index a comparison of the diffusion velocities of the two solutes can be made, if the vol. change on mixing is not too great and if there is no chemical action. The presence of such disturbances is detected by interchanging the solutions. The particular shadow distribution caused by the disturbance is not reversed. D-Striations thus afford a method for the determination of approx. mol. wts. Equally diffusible substances give no D-striations. Slight differences in n result in a much more complicated shadow distribution. Data are given for the shadow distribution of the D-striations for a no. of pairs of solutions of alcohols and carbohydrates.

M. S. BURR.

Dielectric constants of aqueous potassium chloride solutions. A. ASTIN (Physical Rev., 1930, [ii], **35**, 1428—1429).—Corr. results for the dielectric consts. of 0.00025—$0.01N$-KCl do not differ from that of H_2O within the experimental limits of error (2 in 1000 at $0.001N$ and 6 in 100 at $0.01N$). Uncorrected results show the apparent decrease of dielectric const. reported by other observers. This decrease, which is much larger than that predicted by Hückel, varies with frequency, size of condenser, or dimensions of the leads.

L. S. THEOBALD.

Constitution of solutions deduced from absorption measurements. P. VAILLANT (Compt. rend., 1931, **193**, 654—656).—Absorption measurements are given for λ 4800—5700 on solutions of $CoCl_2$ in presence of EtOH and other chlorides.

C. A. SILBERRAD.

Electrolytic dissociation as revealed by the Raman effect. L. A. WOODWARD (Physikal. Z., 1931, **32**, 777—792).—Raman displacements are absent in solutions of KCl, indicating almost complete dissociation, whilst $HgCl_2$ and $Hg(CN)_2$ show displacements due to the undissociated mol. HNO_3, H_2SO_4, and the HSO_4' ions in solutions of $KHSO_4$ appear to be partly dissociated. For HCl, HIO_3, $CCl_3 \cdot CO_2H$, $CHCl_2 \cdot CO_2H$, NaOH, and KOH the results are inconclusive. A spectrograph of large aperture is described.

A. B. D. CASSIE.

Viscosity of suspensions. J. DUCLAUX and (MLLE.) D. SACHS (J. Chim. phys., 1931, **28**, 511—516).—The val. of K in the viscosity formula $\eta = \eta_0(1 + K\phi)$ is 36 for a Bredig Au hydrosol (cf. K=2.5 for spherical particles). Large vals. of K are not necessarily due to solvation, but are probably related to the shape of the particles, since K=19.2 for particles (0.2—0.3 μ) of SiC, which is not solvated by H_2O, and K=4.6—5.9 for PbI_2 in BuOH, the particles of which approximate less closely to spheres than those of SiC.

J. G. A. GRIFFITHS.

Effect of hydrogen-ion concentration on the measurement of the mean particle size of emulsions. I. C. WEEKS (Physical Rev., 1930, [ii], **35**, 668; A., 1927, 108).—At p_H 7.0 the area of a H_2O-spread emulsion stabilised with Na myristate, palmitate, or stearate is const. for a given pressure and quickly reaches equilibrium; at $p_H < 7.0$ the area increases with time without reaching equilibrium, whilst at $p_H > 7.0$ the area ultimately becomes const., but the equilibrium vals. are large and depend on p_H.

L. S. THEOBALD.

Shape of particles in hydrosols of sodium oleate. P. A. THIESSEN and E. TRIEBEL (Z. physikal. Chem., 1931, **156**, 309—316).—Measurements of the fluxional birefringence of Na oleate hydrosols show that the particles are rod-shaped. The amount of the double refraction increases with concentration or with lowering of temp. The particles also possess a sp. double refraction and are therefore cryst.

F. L. USHER.

Molecular arrangement in soap micelles. P. A. THIESSEN and R. SPYCHALSKI (Z. physikal. Chem., 1931, **156**, 435—456).—X-Ray examination shows the particles in Na soap hydrogels to be cryst. and to consist of neutral, anhyd. salts of fatty acids. The structure is independent of the H_2O content of the system and is identical with that of the corresponding salts when cryst. from org. solvents. H_2O contained in the gel is entirely intermicellary. Observations with threads of Na soaps indicate that the salt mols. are oriented perpendicularly to the long axes of the micelles. The distribution of electric charges on the surface of the micelles is discussed.

H. F. GILLBE.

Formation of a lattice during the sol–gel transition of a colloidal system containing elongated particles. P. A. THIESSEN [with (FRL.) E. TRIEBEL] (Z. physikal. Chem., 1931, **156**, 457—468).—The changes of double refraction and electrical conductivity which occur during the transition of supercooled Na oleate hydrosol to the gel form indicate that the formation of a lattice structure

depends essentially on the size and form of the particles, the mol. orientation, and the distribution of the charges on the surface of the particles.

H. F. GILLBE.

Coagulation of strongly solvated sols by organic substances and salts. IV. B. JIRGEN-SONS (Biochem. Z., 1931, 240, 218—231).—In the coagulation of albumin and caseinogen with $FeCl_3$ or $AlCl_3$ and alcohols, the salts in small concentrations (0.0001—$0.001M$) sensitise, in mean concentrations (0.001—$0.1M$) stabilise, and in high concentrations (0.1—$0.4M$) either sensitise ($FeCl_3$) or stabilise ($AlCl_3$). With $CuCl_2$ and $Cu(NO_3)_2$, small concentrations sensitise and mean concentrations stabilise. The stabilisation is dependent on the alcohol concentration and also varies inversely with the dielectric const. With $MnCl_2$ and $CoCl_2$ small and mean concentrations sensitise and high concentrations stabilise. NaOAc sensitises, whilst Na_2HPO_4 and $K_4Fe(CN)_6$ feebly stabilise the alcohol coagulation of albumin. Glycine, alanine, and carbamide stabilise the coagulation of albumin by $HgCl_2$, $CuCl_2$, and $AlCl_3$. Lower temp. ($-10°$) have no decided influence on the alcohol coagulation in presence of salts. When dil. albumin and starch sols are coagulated in presence of salts with varying amounts of alcohol, the degree of coagulation is not a linear function of the alcohol concentration, each alcohol having a max.; e.g., PrOH with albumin has a sharp max. at $1.6M$ (cf. A., 1929, 507).

P. W. CLUTTERBUCK.

Rapid coagulation of sols. I and II. H. J. C. TENDELOV (Chem. Weekblad, 1931, 28, 634—637, 637—640).—I. An account of the mathematical treatment of the kinetics of sol coagulation developed by Smoluchovski and by Müller, and of the experimental investigation of the equations obtained.

II. A résumé of the work of Tuorila and Müller.

H. F. GILLBE.

Coagulation of egg-albumin by supersonic waves. H. WU and S. C. LIU (Proc. Soc. Exp. Biol. Med., 1931, 28, 782—784).—Coagulation results only in solutions containing dissolved air, H_2, or O_2; it does not occur when CO_2 or H_2S is used and no gas bubbles are formed. CHEMICAL ABSTRACTS.

Anisotropy due to flow in cellulose sols. J. M. PRESTON (Nature, 1931, 128, 796—797).—Flowing cellulose sols in Cu-aq. NH_3 show double refraction, indicating the presence of non-spherical particles. The ageing of cellulose sols in air gives rise to lower double refraction, suggesting a diminution in particle size. L. S. THEOBALD.

Theory of jelly formation. S. PRAKASH (J.S.C.I., 1931, 50, 387—388T).—A brief summary of the author's results (cf. A., 1929, 1008, 1235; 1930, 1114, 1117, 1369).

Electrical method of determining gelation temperature of starch. E. C. McCRACKEN (Physical Rev., 1930, [ii], 35, 1423).—A sudden decrease in resistance occurs at 87—88° when an electric current is passed through a potato. This effect is attributed to a disruption of starch grains. L. S. THEOBALD.

Dependence of osmotic pressure and micellar weight of gelatin solutions on the temperature, i.e., on the previous history of the solution. M. FRANKEL (Biochem. Z., 1931, 240, 149—155).—A solution of pure gelatin gave at 6° a micellar wt. of 53,800 and at 30° of 19,800. The same solution after 500 hr. at 37° gave a wt. of 16,500, whereas the control was 24,000. P. W. CLUTTERBUCK.

Diffusion and cataphoresis of methylene-blue in gelatin. (MLLE.) S. VEIL (Compt. rend., 1931, 193, 768—771).—The spectrophotometric method was used. Diffusion extends gradually (cf. A., 1929, 28), with no discontinuities (cf. A., 1928, 238). Cataphoresis produces marked singularities—a thick accumulation at the anode which moves steadily away, leaving a clear space; then comes a series of thinner bands with finally a thick one at the cathode.

C. A. SILBERRAD.

Contraction caused by hydration of proteins. C. MARIE and N. MARINESCO (Compt. rend., 1931, 193, 736—738).—The contraction on adding 1 c.c. of H_2O of varying p_H to 1 g. of gelatin (Merck's "isoelectric") decreases sharply from p_H 3.5 to the isoelectric point, and then rises more slowly to p_H 8.5, with an arrest around the neutral point. With const. p_H and varying amounts of H_2O the contraction per g. of gelatin diminishes rapidly with increased quantity of H_2O. C. A. SILBERRAD.

Morphology of chemical reactions in gels. V. Theory of periodic reactions. F. M. SCHEM-JAKIN (J. Gen. Chem. Russ., 1931, 1, 455—459).—A drop of liquid is a definite unit of the same order as micelles and crystals; in most cases it is analogous in structure to radial or zonal mono- or poly-crystals. The gel reactions previously described (cf. this vol., 428) can be explained from this point of view, and the nature and dimensions of the figures obtained when a drop of $FeCl_3$ is placed on gelatin containing K_2CrO_4 are predicted. R. TRUSZKOWSKI.

Numerical evaluation of infinite series and integrals which arise in certain problems of linear heat flow, electrochemical diffusion, etc. W. L. MILLER and A. R. GORDON (J. Physical Chem., 1931, 35, 2785—2884).—Mathematical.

L. S. THEOBALD.

Equations of motion in thermodynamics. Y. MIMURA (J. Sci. Hiroshima Univ., 1931, A, 1, No. 2, 117—123).—An attempt to evolve the thermodynamics of systems of varying state by analogy with Hamilton's principle. CHEMICAL ABSTRACTS.

Molecular association. G. G. LONGINESCU (Bul. Chim. pura appl., Bukarest, 1930, 31, No. 4—6, 21—76; Chem. Zentr., 1931, i, 2837).—A discussion.

A. A. ELDRIDGE.

Two-component systems involving compound formation. J. RUSSELL and O. MAASS (Canad. J. Res., 1931, 5, 436—441).—The p, v, T relations suggest that compound formation takes place between gaseous HCl and Et_2O, and between HCl and MeOH; the heats of reaction (const. between 50° and 200°) are 5400 and 9200 g.-cal. per mol., respectively.

R. S. CAHN.

Electrolytic dissociation of acids in salt solutions. I. Dissociation constant and activity relationships of the ions of acetic acid in solu-

tions of certain alkali and alkaline-earth chlorides. II. Dissociation constants and the activity relationships of the ions of some fatty acids in sodium and potassium chloride solutions. E. LARSSON and B. ADELL (Z. physikal. Chem., 1931, 156, 352—380, 381—396).—I. Quinhydrone electrode measurements of the activity coeff. at 18° of the H˙ in $0.01N$-HCl solutions containing Na, K, Sr, and Ba chlorides at various concentrations agree closely with those obtained by Bjerrum and Unmack with the H electrode. The activity relations in solutions of AcOH and NaOAc containing chlorides have been determined by quinhydrone electrode measurements, and the variations of the classical ionisation const. α and of the activity coeffs. of the acid mols. and ions with the salt concentration have been examined. With increase of the chloride concentration to about $0.5M$ α and $-\log \phi$ increase, but thereafter they fall; $-\log \phi$ diminishes in the series $SrCl_2$, $BaCl_2$, NaCl, KCl. The activity coeff. of OAc′ in the salt solutions has been calc. from that of the acid as obtained by partition measurements.

II. Determinations have been made of the ionisation const. and activity functions in chloride-containing solutions of the n-fatty acids to C_7, and of $Bu^\beta CO_2H$, $CMe_3 \cdot CO_2H$, and isohexoic acid. The influence of the constitution of the acids is appreciable only at high salt concentrations. If the CO_2H group is attached to a CH_2 or Me group the val. of $-\log \phi$ in a given salt solution is independent of the no. of C atoms in the chain, but in other cases it assumes higher vals. For all the acids $-\log \phi$ is a max. in $0.5M$ salt solutions, and it is always greater in NaCl solutions than in solutions of KCl. The activity coeffs. of the acid ions have not been determined, as those of the acids are not known.

H. F. GILLBE.

Dissociation constants of bile acids. O. M. HENRIQUES (Acta Path. Microbiol. Scand. Suppl., 1930, 3, 141—149; Chem. Zentr., 1931, i, 3130).—Vals. for aq. solutions were extrapolated from those for aq.-alcoholic solutions of taurocholic, taurocholeic, glycocholic, and glycocholeic acids.

A. A. ELDRIDGE.

Hydrolysis constant of iodine. E. ANGELESCU and V. D. POPESCU (Z. physikal. Chem., 1931, 156, 304—308).—The val. of K ($=[HOI][H\textperiodcentered][I']/[I_2]$) has been derived from the error in the titration of I with $Na_2S_2O_3$ in presence of $NaHCO_3$. K varies with the I concentration from 10^{-10} (large $[I']$) to 1.5×10^{-13} (small $[I']$) at 20°. The thermal equiv. of the hydrolysis is calc. to be $-11,700$ g.-cal. at 25°.

F. L. USHER.

Composition of complex cyanide radicals. IV. Nickel cyanide. K. MASAKI (Bull. Chem. Soc. Japan, 1931, 6, 233—236).—Despite the variations of colour of solutions containing $Na_2Ni(CN)_4$, the complex ion at all concentrations is $Ni(CN)_4''$. The equilibrium const. for the dissociation of the complex into Ni˙˙ and CN′ is 1.8×10^{-14} according to e.m.f. measurements.

H. F. GILLBE.

F. p. of mixtures of sulphuric and nitric acids. W. C. HOLMES, G. F. HUTCHISON, and B. ZIEBER (Ind. Eng. Chem., 1931, 23, 1102—1104).—Further

measurements have been made, in which the concentration of H_2SO_4 in the solvent extends from 100 to 109%; the results are plotted with other available data on triangular co-ordinates and the isothermal lines are indicated. The most effective concentrations of HNO_3 for preventing freezing of H_2SO_4 are 1% for 104.5% H_2SO_4, 4% for 107% H_2SO_4, and 6% for 109% H_2SO_4. Low f. p. occur in all these systems at 10% HNO_3.

E. S. HEDGES.

Amphoteric oxide hydrates, their aqueous solutions and crystalline compounds. XII. Systems undergoing hydrolysis and their aggregation products, with special reference to aqueous aluminium salt solutions. G. JANDER and A. WINKEL (Z. anorg. Chem., 1931, 200, 257—278).—The properties of solutions of easily hydrolysable salts are discussed, with special reference to the aggregation which occurs in molybdate solutions. The diffusion coeff. of $Al(NO_3)_3$ solutions has been determined as a factor of the p_H. It does not vary with the age of the solution, and equilibrium is therefore established rapidly; with rise of p_H to about 3 it remains almost const., but thereafter falls rapidly and continuously, indicating progressive aggregation. Evidence has been obtained of the formation of the complexes $[Al(OH)(NO_3)_2,aq.]_x$ and $(AlO \cdot NO_3)_y$. The course of the aggregation process is probably $Al(H_2O)_6(NO_3)_3 \rightarrow (AlO \cdot NO_3)_8 \longrightarrow AlO \cdot OH$, in analogy with the process in Fe˙˙˙ salt solutions. The complexes probably result from chain formation. The occurrence of aggregation has been confirmed by extinction coeff. measurements.

H. F. GILLBE.

System iron-oxygen. H. SCHENCK and E. HENGLER (Arch. Eisenhüttenw., 1931—1932, 5, 209—214).—The solubility of O_2 in γ-Fe is about 0.2% and in α-Fe about 0.035%. The A3 point is slightly raised and the A4 point slightly lowered by the presence of O_2 in solid solution. There is a gap of miscibility in the liquid phase between 0.22 and 21.5% O at 1519°. In the system FeO–Fe_3O_4 a homogeneous liquid phase is obtained with mixtures containing 23—26% O, but the presence of a eutectic m. p. 1200° in the system has not been confirmed. FeO melts incongruently at 1370° and, after cooling from above 1385°, the presence of well-formed Fe crystals in the mass has been detected micrographically. Wüstite and Fe_3O_4 form a eutectic, m. p. 1300°, with 25.3% O, but the eutectic horizontal extends only over a short range of composition. Pure FeO cannot be produced by prolonged heating in vac. of a stoicheiometric mixture of Fe_3O_4 and Fe. A tentative diagram of the stable and metastable equilibria in the system Fe–O based on the above results together with those of other investigators has been constructed.

A. R. POWELL.

Equilibrium pressure of calcium cyanamide formation. N. KAMEYAMA and S. OKA (J. Soc. Chem. Ind. Japan, 1931, 34, 325—327B).—A mixture of $CaCN_2$, graphite, and CaC_2 heated at 900° evolved CO and N_2 owing to the presence of $Ca(OH)_2$ as impurity. The equilibrium pressures were 5 mm. Hg at 956°, 183.5 mm. at 1200°. According to these data the heat of reaction is 54,800 g.-cal.

Higher vals. found experimentally may perhaps be due to the heat of dissolution of CaC_2 in $CaCN_2$.
C. Irwin.

Ternary system CO–N–H and the component binary systems between —185° and —215° and 0 and 225 atm. T. T. H. Verschoyle (Phil. Trans., 1931, A, 230, 189—220).—For liquid CO log $p=$ $-691\cdot91/T+6\cdot9059-0\cdot006044T$, and for solid CO log $p=-520\cdot85/T+10\cdot7005-0\cdot02923T$ (p in cm.); b. p. —191·47°, triple point —205·03°, m. p. —205·03° $+0\cdot0225p$. The triple point of N_2 is —209·95°, and the m. p. —209·95°$+0\cdot0216p$. Isotherms and the f.-p. curves are given for the CO–N_2 and CO–H_2 systems, and data are given for the ternary system at 30, 90, and 150 atm. and —185°, —195°, and —205°.
H. F. Gillbe.

Equilibrium in binary systems under pressure. I. Experimental and thermodynamic investigation of the system NaCl–H_2O, at 25°. L. H. Adams (J. Amer. Chem. Soc., 1931, 53, 3769—3813; cf. this vol., 40).—The compressibility of aq. NaCl solutions (0—25%) has been determined at pressures between 500 and 12,000 bars at 25°. The "compression," k $[=(V_0-V)/V]$, for H_2O is given by $k=$ $16\cdot362\times10^{-6}P-3\cdot42\times10^{-10}P^2+0\cdot068(1-e^{-0\cdot00042P})$, and k decreases with increasing concentration of the solutions. The calc. vals. of the "fictive" or partial vols. of NaCl in solution increase with pressure except at the highest pressures and concentrations; the vals. for H_2O decrease with increase of pressure. The pressure–concentration equilibrium diagram resembles an inverted temp.–concentration diagram. The solubility of NaCl at 25° rises to a max. (27·6 wt.-%) at 4000 bars and then decreases. Between 8000 and 11,800 bars, NaCl,$2H_2O$ is the stable solid phase, and at higher pressure the solubility of NaCl decreases to 25·4 wt.-% at 16,700 bars, where the curve intersects the freezing pressure curve for ice VI, thus affording a "pressure eutectic." Direct determinations confirm the results of the indirect (thermodynamic) method.
J. G. A. Griffiths.

Calcium aluminates. I. Crystallisation of calcium aluminate solutions at 20°. G. Assarsson (Z. anorg. Chem., 1931, 200, 385—408).—The solid phases in equilibrium at 20° with solutions containing varying proportions of CaO and Al_2O_3 have been investigated. CaO,H_2O is not found, although present in cements. $Al_2O_3,3—4H_2O$ is deposited in isotropic grains, in flakes adhering to the walls, or as an amorphous gel. The aluminates identified were : $4CaO,Al_2O_3,13\cdot5H_2O$ (not $12H_2O$ as stated by previous workers); $3CaO,Al_2O_3,12\cdot5H_2O$; $3CaO,Al_2O_3,6H_2O$; and $2CaO,Al_2O_3,8(?)H_2O$. Optical and chemical characters are given. In solutions containing <50 mg. CaO per 100 c.c. the solubility decreases with increasing proportion of CaO. The results are shown in a triangular diagram.
F. L. Usher.

Reciprocal salt pair $MgCl_2$–$NaNO_3$–H_2O. II. A. Sieverts and E. L. Müller (Z. anorg. Chem., 1931, 200, 305—320).—The 75° and 110° isotherms have been determined. The solid phases at these temp. are NaCl, $NaNO_3$, $MgCl_2,6H_2O$, $MgCl_2,4H_2O$, $MgCl_2,2H_2O$ (110° only), $Mg(NO_3)_2,6H_2O$ (75° only),

and $Mg(NO_3)_2,2H_2O$. No double salts exist. The transition temp. of $MgCl_2,4H_2O \rightleftharpoons MgCl_2,2H_2O$ (181·5°) is reduced to below 110° by the presence of $Mg(NO_3)_2$, and that of $MgCl_2,6H_2O \rightleftharpoons MgCl_2,4H_2O$ (116·7°) to below 75°. Attempts to isolate the lower hydrates of $MgCl_2$ and $Mg(NO_3)_2$ are described.
H. F. Gillbe.

Heat of dissociation of oxygen. J. Kaplan (Physical Rev., 1930, [ii], 35, 436).—The heat of dissociation is $5\cdot7\pm0\cdot1$ volts.
L. S. Theobald.

Atomic number and heat of formation. W. A. Rothbraunschweig (Naturwiss., 1931, 42, 860).— The heats of formation of the oxides of C, Si, Ti, Zr, Hf, and Th are plotted against the at. nos.
A. B. D. Cassie.

Thermodynamics of the synthesis of methyl alcohol from water-gas. A. V. Frost (J. Gen. Chem. Russ., 1931, 1, 367—376).—The free energy of the reaction $CO+2H_2 \rightleftharpoons MeOH$ is $-\Delta F/4\cdot573T=$ $\log K(RT)^2=3925/T-9\cdot840\log T+0\cdot00347T+14\cdot8$. The val. calc. on the basis of Nernst's heat theorem differs from the experimental val. by $+1\cdot04\pm0\cdot4$, whilst for other reactions the discrepancy is, according to Eucken and Fried's figures, $+0\cdot9$.
R. Truszkowski.

Conductivity and dielectric constant of electrolyte solution at high frequency. M. Wien (Ann. Physik, 1931, [v], 11, 429—453).—Using the Barett method (cf. this vol., 801) the conductivities and dielectric consts. of $MgSO_4$ and $Ba_3[Fe(CN)_6]_2$ solutions have been measured at wave-lengths of 10, 20, and 40 m., and those of $Ba_3[Fe(CN)_6]_2$ and Li_2SO_4 at 10 and 20 m., respectively, for equiv. concentrations up to 5×10^{-2}. The results are in agreement with the Debye–Falkenhagen theory.
J. W. Smith.

Mobility of some ions containing iron. IV. Nitroprusside ion. F. Hölzl and W. Stockmair (Monatsh., 1929, 52, 289—294; cf. A., 1930, 1253, 1524).—Conductivity and transport measurements of solutions of Na, K, NH_4, Rb, and Ba nitroprussides give 69·45 for the mobility of the ion $[Fe(CN)_5NO]''$.
M. S. Burr.

Temperature coefficient of the antimony electrode. II. G. P. Avsejevitsch and I. I. Shukov (Z. Elektrochem., 1931, 37, 771—775).— The stability of the electrode (cf. A., 1929, 899) is largely dependent on the condition of the electrodeposited Sb, and experiments have therefore been made with various org. solvents for the $SbCl_3$. A steady potential is obtained only if the deposit is of the greyish, matte type. Solutions in HCO_2H, MeCN, and $PhNO_2$ yield a smooth deposit for which the potential is unstable, whilst MeOH solutions yield a deposit of suitable structure but of less satisfactory behaviour than that obtained with $COMe_2$ solutions. By final anodic polarisation of the electrode in dil. H_2SO_4 a reproducible, stable electrode is obtained. The p_H of a solution for which the electrode potential (N-calomel electrode) is E at $T°$ is given by $p_H=$ $\{E-0\cdot1-(T-18)0\cdot00025\}/\{0\cdot0542+(T-18)0\cdot000275\}$.
H. F. Gillbe.

Use of saturated ammonium chloride in the elimination of contact potentials. C. N. Murray and S. F. Acree (Bur. Stand. J. Res., 1931, 7, 713—

721).—Liquid junction potentials may be reduced to $\pm 1 \cdot 0$ mv. by the use of saturated solutions of NH_4Cl, which is considered superior to KCl by reason of its greater mol. solubility. The p_H of the solution must be sufficiently low to avoid errors due to liberation of NH_3. Preliminary experiments on the use of RbBr, $LiIO_3$, and NH_4ClO_4 for the purpose have been carried out. E. S. HEDGES.

Isothermal metallic cells. O. SCARPA (Mem. R. Accad. Ital., Sci. Fis. Mat. Nat., 1930, **1**, Chim., No. 5, 26 pp.; Chem. Zentr., 1931, i, 2848).—Metallic cells can produce a current when two metals in contact form a solution or compound. The e.m. f. of the cells: $Cu|Hg|Zn|Cu$ ($0 \cdot 7 \times 10^{-6}$ volt at 15°); $Cu|Hg|Cd|Cu$ ($1 \cdot 10 \times 10^{-6}$ volt at 15°); $Cu|Hg|Zn-Hg|Cu$; and $Cu|Hg|Cd-Hg|Cu$ have been measured. Vals. of the last two depend on the concentration of the amalgam. The theoretical aspect of the phenomenon is discussed. A. A. ELDRIDGE.

Electrochemical investigation of solid silver-gold alloys. A. ÖLANDER (J. Amer. Chem. Soc., 1931, **53**, 3577—3588).—The e.m.f. of the cell $Ag|AgCl,KCl|Ag$, $0 \cdot 015$—$0 \cdot 75$ mol. fraction Au has been determined between 707° and 1207° abs. With mol. fractions of Au $> 0 \cdot 75$, large drifts of e.m.f. are observed. Activity coeffs. of Ag, as well as partial molal heats and entropies of mixing are calc. Phases of low entropy exist below 800° with 0—18 at.-% of Au and with > 50 at.-% of Au. A phase diagram is suggested. J. G. A. GRIFFITHS.

Oxidation–reduction of pyocyanine. II. Redox potentials of pyocyanine. B. ELEMA (Rec. trav. chim., 1931, **50**, 1004).—The equation previously given for E_h (cf. this vol., 1013) is incorrect; an improved method for showing the marked drop of potential at 50% reduction for high vals. of the equilibrium const. is given. N. H. HARTSHORNE.

Anodal polarisation of smooth and platinised platinum. V. V. PITSCHETA (J. Gen. Chem. Russ., 1931, **1**, 377—387).—The potential at Pt anodes during the passage of a current depends on the formation of a film of O_2 or suboxide. When the current is broken the potential depends on the accumulation of at. O. The behaviour of a given anode is profoundly affected by its previous history, and reproducible results are obtained only under strictly uniform conditions. The depolarisation potentials are inversely proportional to the current density for both smooth and platinised Pt. R. TRUSZKOWSKI.

Relations between galvanic and voltaic potential and ionic adsorption as determining potential. M. ANDAUER and E. LANGE (Z. physikal. Chem., 1931, **156**, 241—257).—A thermodynamic treatment of the relation of the three types of potential to the concentration of ions in an electrolyte in the case of conducting electrodes. F. L. USHER.

Temperature measurements at working electrodes. VI. B. BRUŽS (Z. physikal. Chem., 1931, **156**, 279—290; cf. this vol., 435).—The partial molal entropies of $Cu^{\cdot\cdot}$ in solutions of $CuSO_4$, viz., $27 \cdot 8$, $25 \cdot 1$, and $20 \cdot 7$ g.-cal. per 1°, for mol fractions $0 \cdot 018$, $0 \cdot 004$, and $0 \cdot 0004$, respectively, have been calc. from

the Peltier effect at Cu electrodes measured by means of a calorimeter which is described in detail. F. L. USHER.

Copper depositing potentials in complex solutions of cuprous halides. N. THON and J. PINILLA (Compt. rend., 1931, **193**, 661—664).—Current density-cathode potential curves for the deposition of Cu from solutions of CuX (X=Cl, Br, I, or CNS) in aq. MX+ nHX (M=alkali metal) are all similar. Those for X=Br are discussed. For low current density the potential is relatively positive, then follows an arrest, after which it increases rapidly, whilst the potential decreases but slightly. The arrest is due to the reaction $Cu^{++} + \ominus \longrightarrow Cu^+$; this with increased current density is overbalanced by $Cu^+ + \ominus \longrightarrow Cu$, which requires a lower potential. C. A. SILBERRAD.

Anode phenomena in the electrolysis of potassium acetate solutions. II. Discharge potential of the acetate ion. S. N. SHULK and O. J. WALKER (Trans. Faraday Soc., 1931, **27**, 722—730).—At a smooth Pt anode C_2H_6 and CH_4 are produced only above a crit. anode potential; this is $2 \cdot 14$ volts up to $2N$, but decreases in more conc. solutions. The ratio CH_4/C_2H_6 increases with concentration but decreases rapidly with increasing current density. C. W. DAVIES.

Application of theory of similarity to chemical phenomena. I. Y. HORI (J. Soc. Chem. Ind. Japan, 1931, **34**, 388—391B).—Theoretical. E. S. HEDGES.

Effective (molecular) cross-sections in gas reactions. J. SCHAY (Z. physikal. Chem., 1931, B, **14**, 237—240).—Theoretical. In gas reactions which are bimol. in both directions the effective mol. collision cross-sections for the forward and reverse changes are of the same order of magnitude. Their ratio appears not to depend on the heat tone of the reaction. N. H. HARTSHORNE.

Rationale of movement of flame through explosive mixtures of gases. I. Explosions in closed containers. O. C. DE C. ELLIS (J.S.C.I., 1931, **50**, 403—409T).—It is shown with the aid of timed snapshot photographs that all flame movement may be reduced to a simple meteorological basis. The flame surface is an isobaric boundary between two winds of opposite direction. The outward wind, taken with the lie of the gas space, controls the shape and displacement of the flame. In multiple ignitions, it forms nodal calms. The inward wind is the mode of compression of the ignited gases, which continue their combustion, often with luminance, as "after-burning." Tracts of wall where the flame surface touches act as anchors, since they not only stop the production of pressure, but also act as pressure drains. Wind movements that increase the area of the flame surface, thereby increasing the rate of combustion and of energy release, and this is the rôle of motion and turbulence in increasing the speed of the flame by distorting it.

**Oxidation of fuel vapours in air. I. Carbon disulphide and carbon monoxide. II. Hydrogen, methane, and coal gas. III. Comparative studies of (a) ethane and ethylene, (b) pent-

anes and amylenes, (c) ethyl and amyl alcohols, (d) acetaldehyde and valeraldehyde. IV. Aromatic hydrocarbons, cyclohexane and cyclohexene. V. Acetylene. E. W. J. MARDLES (Trans. Faraday Soc., 1931, 27, 681—721; cf. A., 1928, 597).— Results are recorded for the pressure changes accompanying the slow reaction in fuel–air mixtures at various concentrations, the min. temp. at which oxidation is appreciable after 20 sec., the available O_2 consumed in this time at various temp., the composition of the products, and the effect of solid and gaseous inhibitors. The pressure changes are complex; usually there is an initial decrease, not detectable at the higher temp., followed by a rise. The temp. of initial combustion normally shows a min. for approx. 50% mixtures, but for CS_2 rises throughout with increasing mixture strength. The temp. coeff. is markedly greater for the paraffins than for the other compounds. Metal surfaces may raise or lower the temp. of initial combustion, but " antiknock " properties are always associated with a reduced temp. coeff. and a reduced yield of aldehyde in the products. Theories of combustion are discussed; it is held that the primary stage is the formation of a peroxide. C. W. DAVIES.

Flow method for measuring the velocities of gas reactions. E. W. R. STEACIE and H. A. REEVE (Canad. J. Res., 1931, 5, 448—454).—A method for measuring the velocities of gas reactions by pressure changes is found, when tested by the decomp. of NH_3 on a SiO_2 surface, not to be very sensitive. R. S. CAHN.

Kinetics of thermal chlorination of methane. R. N. PEASE and G. F. WALZ (J. Amer. Chem. Soc., 1931, 53, 3728—3737).—The reaction has been investigated dynamically between 225° and 285°. The rate of chlorination is proportional to the product $[Cl_2][CH_4]$ in the absence of O_2. O_2 strongly retards the reaction and the velocity is approx. proportional to $[Cl_2]^2/[O_2]$ and independent of $[CH_4]$. " Packing " the reaction vessel with glass tubing or altering the nature of the surface has relatively small effects. Thus, the reaction is predominantly homogeneous and of the "chain" type. The temp. coeffs. indicate an energy of activation 77,300 g. cal. with 1% O_2 and 31,600 g.-cal. without O_2. A difficulty in assigning a mechanism similar to that of the photo-chemical H_2-Cl_2 reaction is indicated. J. G. A. GRIFFITHS.

Reaction between oxygen and ethylene. I. II. S. LENHER (J. Amer. Chem. Soc., 1931, 53, 3737— 3751, 3752—3765; cf. A., 1929, 1243; this vol., 1031).—I. A $C_2H_4+O_2$ mixture was passed through a cylindrical pyrex vessel (vol. 65 c.c.) at temp. between 360° and 410°; some CO_2 and H_2 were produced, but the main products were CO and material condensed in solid CO_2. The condensate contained ethylene oxide, glycol, glyoxal, CH_2O, HCO_2H, and H_2O. The yield of all products decreases to different extents with increasing rate of flow. The reaction is stopped at temp. <500° by " packing " the vessel, and at 500° the oxidation is at the surface and affords mainly CO, CO_2, and H_2O. 3—5% HNO_3 vapour does not catalyse the homogeneous reaction, but C_2H_4 reduces NO at 295° (cf. this vol., 1133). In dynamic experiments with large vessels (vol. 960 c.c.) no glyoxal was detected, but dihydroxymethyl peroxide was a principal product, probably formed by oxidation of CH_2O with H_2O_2 produced in the reaction. The yield of $C_2H_6O_4$ and formic acid is decreased and that of CH_2O is increased in SiO_2 vessels, and $C_2H_6O_4$ is absent from the products from vessels of Al, Fe, or pyrex coated with KCl or K_2SiO_3. The results indicate that although the reaction is mainly homogeneous, the surface has an important effect on its course.

The oxidation of propylene at 280—315° affords products similar to those from C_2H_4.

II. With a re-circulating system at temp. between 410° and 600°, and short times of contact with C_2H_4-10%O_2 mixtures, the principal products are ethylene oxide and CH_2O, but the yields decrease at the higher temp. and some MeCHO is formed probably by thermal rearrangement of C_2H_4O. At 450°, the polymerisation of C_2H_4, mainly to propylene and a little butylene, becomes prominent and increases with rise of temp.; O_2 catalyses the reaction. The primary process of the oxidation probably consists of the activation of C_2H_4 with the formation of a peroxide leading to the production of C_2H_4O, and also the direct oxidation of C_2H_4 to CH_2O. The other products appear in subsequent steps.
J. G. A. GRIFFITHS.

New series of homogeneous unimolecular gas reactions. C. C. COFFIN (J. Amer. Chem. Soc., 1931, 53, 3905—3906).—Preliminary. Gaseous decomps. represented by the equation $R'''CO_2 \cdot CHR' \cdot CO_2R'' \longrightarrow R'CHO + R'''CO \cdot O \cdot COR''$ are homogeneous and unimol. J. G. A. GRIFFITHS.

Hydration of metaphosphates in neutral and acid solution. S. S. DRAGUNOV and A. N. ROSSNOVSKAJA (Z. anorg. Chem., 1931, 200, 321—331).— Both in neutral and in acid solution $NaPO_3$ combines with H_2O to give orthophosphate only. The reaction appears unimol., but the velocity coeff. decreases with time owing to the inhibiting influence of the orthophosphate formed. $(NaPO_3)_6$ in neutral solution also gives rise to orthophosphate only, but in acid solution pyrophosphate is also formed. F. L. USHER.

Kinetics of the iodometric oxidation of thiocyanate. E. ANGELESCU and V. D. POPESCU (Z. physikal. Chem., 1931, 156, 258—278).—In presence of $NaHCO_3$ the reaction determining the observed velocity is bimol. between CNS' and OI', but in practice it appears unimol. on account of the extremely small concentration of OI' compared with that of CNS'. The I' produced in the reaction acts as a negative catalyst. In presence of NaOH the slowest of the single reactions is the hydrolysis of ICN. The oxidation is practically instantaneous when NH_3 or NH_4 borate is used as the alkali, because under these conditions the concentration of OI' is greatly increased and the ICN is not hydrolysed. F. L. USHER.

Oxidation velocity of sodium sulphite and velocity of dissolution of oxygen in water. S. MIYAMOTO, T. KAYA, and A. NAKATA (J. Sci. Hiroshima Univ., 1931, A, 1, No. 2, 125—145).—Measurement of the velocity of oxidation of Na_2SO_3 provides a method for determining the initial rate of dissolution of O_2 in H_2O. The velocity coeffs., calc. as zero order

reactions, were a linear function of the air velocity. The oxidation velocity was also proportional to the partial pressure of O_2. The threshold val. of the velocity components vertical to the surface, above which mols. of O_2 can enter the liquid phase, is calc. to be 1.65×10^5 cm. per sec., independently of temp. between 15° and 35°. CHEMICAL ABSTRACTS.

Period of induction of chemical reactions. II. Action of hypophosphorous acid on sodium iodate. P. NEOGI and B. SEN (J. Indian Chem. Soc., 1931, 8, 725—737).—When H_3PO_2 and $NaIO_3$ are mixed the time which elapses before the appearance of I is unaffected by light, but depends on the concentration of the reactants. $K = T \times C_h \times C_i$, where K is a sp. const., T the period of induction, and C_h and C_i are the concentrations of the two salts, respectively. Rise in temp. causes a decrease in T, as also does the addition of the following substances : MeOH, CCl_4, C_6H_6, CS_2, o-, m-, and p-xylene, $CHCl_3$, dil. mineral acids, S sol, reducing agents, finely-divided metals, Pt-black, and animal charcoal. $Na_2S_2O_3$ causes a marked diminution of T and even complete disappearance if sufficiently conc.; NH_4CNS, $Na_2S_4O_6$, and KI act similarly. T increases in presence of EtOH, $Pr^\beta OH$, n- and iso-BuOH, $C_3H_5(OH)_3$, Cl′, SO_4'', NO_3', citrates, tartrates, dextrose, lævulose, mannose, d- and l-tartaric acids, and maleic and fumaric acids, l-tartaric and fumaric acids having more influence than their optical isomerides. $Pr^a OH$ totally inhibits the reaction, whilst sucrose has no action and oxidising agents have very little. The crit. val. of C_i at which T disappears, for a fixed val. of C_h of $0.0172M$, is $0.9130M$. M. S. BURR.

Velocity of hydrolysis of acyl derivatives of glyoximes. M. MILONE (Atti R. Accad. Sci. Torino, 1931, 66, 59—66; Chem. Zentr., 1931, i, 3113).—The Ac_2 and Bz_2 derivatives of α-benzildioxime were hydrolysed 6 times as rapidly as those of the β- and 3 times as rapidly as those of the γ-form. The Ac_2 derivatives have m. p. 148°, 125°, and 115°, and the Bz_2 derivatives m. p. 220°, 159°, and 135°, respectively. A. A. ELDRIDGE.

Thermal constant and temperature coefficient of fermentation by expressed yeast juice and yeast maceration juice. S. KOSTYTSCHEV and G. MEDVEDEV.—See this vol., 1457.

Dependence of reaction velocity on surface and agitation. III. Experimental study of agitation. A. W. HIXSON and J. H. CROWELL (Ind. Eng. Chem., 1931, 23, 1160—1169).—The consts. obtained by application of the cube-root law to dissolving systems form criteria of the intensity of the agitation accompanying the process. The idea of a standard agitation has been developed and applied to the investigation of the dissolution of salts in H_2O; the effects of all the known variables have been studied. E. S. HEDGES.

Rate of dissolution of a granular solid. K. M. WATSON (Ind. Eng. Chem., 1931, 23, 1146—1151).—Fick's law of diffusion is developed to express the rate of dissolution of a granular solid as a function of temp., concentration, particle size, and rate of movement. An apparatus for the quant. study of rates

of dissolution, in which a thin layer of the solid charge is contained in a short chamber through which the solvent may be passed at a const. rate, is described. The coeffs. and functions of the proposed equations have been evaluated for the dissolution of $Na_2CO_3,10H_2O$ in H_2O. E. S. HEDGES.

Dissolution of metals in acids. J. N. BRÖNSTED and N. L. R. KANE (J. Amer. Chem. Soc., 1931, 53, 3624—3644; cf. A., 1928, 717; 1930, 1530).—The rate of dissolution of approx. $0.024M$-Na amalgam in aq. solutions of $p_H > 7.5$ has been investigated at 18° by the pressure of H_2 produced. The rate of reaction is directly proportional to the square root of Na concentration, and hence the reaction is completed in a finite time. The rate of reaction with aq. NaOH is slow and not reproducible. With phosphate, glycine, and PhOH buffers of const. [H·], the velocity increases linearly with buffer concentration. Conductivity effects are absent. The results support the view that the dissolution of a pure metal (e.g., Na) is due to reaction between an electron in the metal and a mol. of the acid. This idea conforms with the extended theory of acids and bases. The reactivity const. of the acids tend to increase with the strength of the acid, but other effects intervene. The presence of $0.0001M$-$[Co(NH_3)_5H_2O]^{...}$ in the glycine buffers greatly accelerates the reaction; higher concentrations lead to violent reaction and a deficiency of evolved H_2. The result is explained as an effect of the high positive charge and the resultant strong attraction for electrons. The great strength of the H_3O^+ ion is correlated with its extreme speed of reaction, and the dissolution of Na in strong acids is governed chiefly by the velocity of the diffusion process. The rate of reaction of Na with PhOH in C_6H_6 is proportional to the concentration of PhOH and the reaction const. of the latter is much higher than in H_2O. J. G. A. GRIFFITHS.

Compounds of the system CaO–FeO and their rôle in Portland cement. II. J. KONARZEWSKI (Rocz. Chem., 1931, 11, 607—635; cf. this vol., 1010). —Ca ferrites are formed from $CaCO_3$ and Fe_2O_3 at temp. $>500°$. The reaction takes place in the solid phase, its velocity being given by $y^2 = 2kt$, where y is % transformation and t is time, and the effect of temp. on k is given by $k = e^{B - Q_A/RT}$. The curve connecting $\log y$ with t consists of two intersecting straight lines; this is due to the fact that at lower temp. $CaCO_3$ reacts directly with Fe_2O_3, whilst at above 900° CaO is formed, which also reacts with Fe_2O_3. The velocity of reaction also depends on the degree of comminution of the substrates. H_2O has little action on $2CaO,Fe_2O_3$. The reduction of $2CaO,Fe_2O_3$ in H_2 commences at about 500°, the ratio Fe : FeO in the product increasing with rise in temp. $2CaO,Fe_2O_3$ does not decompose below 1400°. CaO forms a compound with FeO, probably $2CaO,FeO$. $2CaO,Fe_2O_3$ is the only ferrite possessing cementing properties, and it is probable that this compound exerts a favourable effect on the binding of cement. The addition of Fe_2O_3 to Portland cement facilitates the grinding and burning of the raw material and enhances the strength of the product. R. TRUSZKOWSKI.

Determination of speed of combustion of colloidal powder. H. MURAOUR (Technique mod., 1931, 23, 177—185; Chem. Zentr., 1931, i, 2712) — Calculation by the usual method, from $(\delta p/\delta t)_{max.}$, may lead to substantial errors. The surface $fp\delta t$ corresponding with the pressure–time curve is therefore determined by evaluation of $P_{max.}/x$; $x = \Delta \log p/\Delta t = tg\alpha$. By the use of a Krupp bomb (700 g. charge) the speed of combustion of uniform powders may be readily determined.　　A. A. ELDRIDGE.

Topochemistry of corrosion and passivity. I. E. PIETSCH and E. JOSEPHY (Z. Elektrochem., 1931, 37, 823—838).—The electrochemical theory of corrosion is considered to be inadequate. A theory is evolved, according to which the primary process of corrosion consists in adsorption at active discontinuities in the surface of the metal, and is developed on the lines of quantum mechanics, with application to heterogeneous catalysis, the catalytic influence of ions on corrosion, and the phenomena of passivity and overpotential.　　E. S. HEDGES.

Surface reaction between ethylene and the halogens. R. B. MOONEY and H. G. REID (J.C.S., 1931, 2597—2605).—The reaction between C_2H_4 and I to form $C_2H_4I_2$ occurs at 30° at the surface of I crystals, the rate (measured manometrically) being proportional to the C_2H_4 pressure. A glass surface covered with EtOH has an activity comparable with that of I, but glass and paraffin are inactive. The heat of activation (from temp. coeff.) is $19\cdot8\pm3$ kg.-cal. C_2H_4 and $(CN)_2$ do not react on glass at 150°, or on SiO_2 gel at 110°. CNCl and CNBr do not react with C_2H_4 at 37°, but CNI and C_2H_4 give $C_2H_4I_2$ and $(CN)_2$.　　H. J. EMELÉUS.

Kinetics of the catalytic hydrogenation of ethylene. C. SCHUSTER (Z. physikal. Chem., 1931, B, 14, 249—264).—The rate of the reaction $C_2H_4 + H_2 = C_2H_6$ at the surface of activated charcoal, containing about 3% of Fe and a trace of Cu, between $-84°$ and $50°$ at low pressures depends only on the H_2 pressure (to which the H_2 surface concentration is almost directly proportional) unless the surface concentration of the C_2H_4 is below $0\cdot4$—$0\cdot5$ c.c. per g., in which case it depends also on this. It is concluded that the reaction occurs only at active centres, which are saturated with C_2H_4 so long as the surface concentration of this gas is not below the above crit. val. They may be the metallic atoms present, since the number of these is of the same order as the number of centres calc. from this crit. val. At 75° and, towards the end of the reaction, at 50° the rate is best represented by the equation $dx/dt = K(a-x)^{1\cdot5}$, the symbols a and x referring to H_2, and this is attributed to the altered form of the H_2 adsorption isotherm at higher temp. The heat of activation between $-84°$ and $50°$ is 2000 ± 500 g.-cal., and this low val. may be explained either by the reaction rate being governed by the rate of diffusion of H_2 on the charcoal towards the active centres, or, if it be assumed that the reactants can remain in contact for a long time, by the theory of Born and Weisskopf (this vol., 576, 918).　　N. H. HARTSHORNE.

Synthesis of carbamide from ammonium carbamate. B. NEUMANN and A. SONNTAG (Z. Elektrochem., 1931, 37, 805—812).—The formation of $CO(NH_2)_2$ from $NH_2\cdot CO_2NH_4$ by heating in a steel bomb lined with Sn–Pb alloy increases rapidly and the yield is higher as the temp. is raised from 135° to 155°. Addition of Al_2O_3 or FeO for the purpose of removing the H_2O produced in the reaction does not improve the yield, but has the reverse effect. Since the equilibrium is altered, these substances cannot be considered as catalysts, although the velocity of reaction is increased, and they appear to act by lowering the m. p. of the mixture, thus favouring reactions in the liquid phase. Other addenda used technically probably act in the same way.　　E. S. HEDGES.

Energy transformations at surfaces. III. **Influence of polar adsorption on the rate of hydrogenation of dyes.** H. KAUTSKY and W. BAUMEISTER (Ber., 1931, 64, [B], 2446—2457; cf. this vol., 1353).—Silicic acid gel is combined with $[Pt(NH_3)_4]^{++}$ ions by polar adsorption and the adsorbate after desiccation in vac. is reduced by H_2 at 360°. A Th hydroxide–Pt catalyst, obtained by adsorption of $[Pt(OH)_6]^{--}$ ions and reduction at 120—150°, is also used. The rate of hydrogenation of methylene-blue in presence of these catalysts, the former of which adsorbs whereas the latter does not adsorb methylene-blue from aq. solution, is determined. The velocity is extraordinarily restricted by polar adsorption, the effect being more marked with diminution of the concentration of the solution which is in equilibrium with the amount of methylene-blue on the surface. Only that portion is hydrogenated which is dissolved in H_2O and reaches the Pt of the catalyst to be thereby adsorbed. With insol. polar adsorbed dyes the rate of hydrogenation is immeasurably small. Within the surface there is no marked diffusion of the polar adsorbed dye mols. among themselves or with the catalytically active regions and hence no direct interaction. The interchange of mols. occurs through the solution.　　H. WREN.

Acid and salt effects in catalysed reactions. XXV. **Catalytic effects in the intramolecular transformation of phorone.** H. M. DAWSON and E. SPIVEY (J.C.S., 1931, 2658—2665).—The catalytic effect of HCl, AcOH, and acetate buffers on the change of phorone preceding its reaction with I was measured at 25° in 50% EtOH solution. The dissociation const. of AcOH in 50% EtOH is $2\cdot7\times10^{-6}$. The autocatalytic reaction was studied. The catalytic effect of the solvent medium was large in the early stages.　　H. J. EMELÉUS.

Action of sodium hypophosphite on aqueous solutions of cobalt salts. C. PAAL and L. FRIEDERICI (Ber., 1931, 64, [B], 2561—2569).—In contrast to the behaviour of Ni solutions (this vol., 1019), aq. solutions of $CoCl_2$ are not reduced by NaH_2PO_2 even in presence of small amounts of Pd. In aq. NH_3 in presence or absence of catalyst reduction occurs with production of Co and a little Co phosphide. Addition of Pd accelerates the change, and with relatively large amounts of catalyst Co free from

phosphide is obtained. $CoCl_2$ in presence of alkaline Na K tartrate, even without Pd, yields mainly Co with a little Co phosphide. Reduction does not occur when $CoCl_2$ in presence of an excess of NaOAc is warmed with NaH_2PO_2, and addition of Pd affords salt-like materials containing Co, P, and O. Treatment of mixtures of Co and Co phosphides with HCl leaves a residue richer in P than the original material, but the phosphide is simultaneously attacked to a marked extent. H. WREN.

Influence of solvents on chemical reactions. I. Reaction between trichloroacetic acid and ethyl diazoacetate in hydrocarbon solvents, and the influence of additions. A. WEISSBERGER and J. HÖGEN (Z. physikal. Chem., 1931, **156**, 321—351).— The predominant reaction between $CCl_3 \cdot CO_2H$ and Et diazoacetate in non-hydroxylic solvents at 0—10° is bimol. and yields N_2 and an ester of glycollic acid. The temp. coeff. in C_6H_{14} and C_7H_8 is 1·7. Although satisfactory vals. of the velocity coeff. k are obtained with an equimol. solution of the reactants or with an excess of acid, if an excess of ester is present k falls rapidly with decrease of the acid concentration. The effect is caused by the formation of a mol. complex between the reactants. The influence of various additions to the solution has been studied. k is depressed by Et_2O, $COMe_2$, alcohols, menthone, and $NHPh_2$, and, to a smaller extent, by acetophenone and benzophenone. Anisole, Ph_2O, C_6H_6, NPh_3, and tribromoaniline are without influence. The retarding influence is due to combination of the added compound with the acid, and its extent may be regarded as a measure of the affinity between the acid and the compound. H. F. GILLBE.

Temperature coefficient of reactions catalysed by acids and bases. M. KILPATRICK, jun., and M. L. KILPATRICK (J. Amer. Chem. Soc., 1931, **53**, 3698—3710; cf. A., 1928, 848; 1930, 300).—The catalysis of the mutarotation of α-glucose has been investigated dilatometrically in 0—0·25M-HCl, acetate–AcOH, and pyridine–pyridinium chloride buffers. Catalytic consts. for H˙, AcO′, and pyridine have been evaluated, and the following heats of activation have been calc. from the temp. coeff.: H˙ 19,300 g.-cal., AcO′ 19,100, pyridine 18,000, and H_2O 17,600. Generalising from the results, little change in the relation between catalytic strength and relative acid strength is to be expected with change of temp. in the mutarotation of glucose.

J. G. A. GRIFFITHS.

Transformation of green into violet modifications of chromium sulphate. S. I. ORLOVA and N. N. PETIN (J. Gen. Chem. Russ., 1931, **1**, 345—358).—The spontaneous transformation of green into violet solutions of $Cr_2(SO_4)_3$ is accelerated by H˙ or SO_4'', and is represented by $[Cr_4O_4(SO_4)_4]SO_4 + H_2SO_4 \rightleftharpoons 2Cr_2(SO_4)_3 + H_2O$. This equation also explains the acceleratory effect on the velocity of crystallisation of the addition of acids to Cr alum solutions.

R. TRUSZKOWSKI.

Thiol compounds as anti-catalysts in oxidations with molecular oxygen. II. Oxidation of thiol compounds with hydrogen peroxide. A. SCHÖBERL (Z. physiol. Chem., 1931, **201**, 167—

190; cf. this vol., 691).—Previous work is confirmed. The anti-catalytic action of SH-compounds holds also with $SH \cdot CH_2 \cdot CO_2H$. The disulphide compounds of SH-glutathione (SS-glutathione, $[\alpha]_{5461}^{22}$ −115·6°) and of $SH \cdot CH_2 \cdot CO_2H$ are readily obtained by oxidation with H_2O_2; they are inactive. This confirms the slow inactivation of the anti-catalyst as being due to oxidation by H_2O_2 produced in the reaction.

J. H. BIRKINSHAW.

Autoxidation of benzaldehyde. Action of anti-oxygenic compounds and applications. Oxidation of ethylenic compounds. E. RAYMOND (J. Chim. phys., 1931, **28**, 480—510; cf. A., 1930, 1582). —Bertram's purification of oleic acid is modified (A., 1927, 750). Traces of H_2O, H_2SO_4, NaOH, and NH_3 are anticatalysts in the autoxidation of PhCHO. The velocity of autoxidation of PhCHO in the presence of oleic acid, esters of ethylenic acids, ethylenic hydrocarbons and alcohols, and cyclic compounds is given by $v = e^{-Kc}$, where c is the concentration of and K is characteristic of the anticatalyst. K is greatly influenced by the nature and position of the various groups relative to the ethylenic linking. Proximity and multiplicity of C_6H_6 nuclei and multiplicity of ethylenic linkings greatly increase K, which is largely diminished by CO_2H and OH. *trans*-Compounds are more active than *cis*.

BzO_2H formed in the oxidation of PhCHO oxidises dissolved substances, and good yields of the ethylenic oxides of oleic acid, stilbene, styrene, and squalene have been obtained. J. G. A. GRIFFITHS.

Catalytic action of surfaces. J. E. NYROP (Chem. and Ind., 1931, 752—755).—Starting from Sommerfeld's theory of the state of free electrons in conductors, the conditions for the existence of an atm. of rapidly-moving electrons in the immediate vicinity of a metallic surface are worked out and catalytic phenomena are explained by assuming chemical reactions to be promoted by these electrons. If various mols. are brought in between the surface electrons, electronic impact may ionise or activate the mols., forming ions which are able to produce new mols. by collision with other ions or mols. Such new mols. may also be ionised and thereby adsorbed, but some of them will leave the surface zone. A catalytic process is thereby produced. If new mols. are not formed, ordinary adsorption takes place. If mols. having a low energy of ionisation are also present they will preferentially occupy the zone and thereby hinder the catalytic process, thus having a "poisoning" action. The following laws governing catalytic processes are deduced: (1) The catalytic effect of a surface depends on the max. kinetic energy of the "free" electrons of the catalyst. (2) If the ionisation energy of a mol. is lower or becomes lower close to the surface than the kinetic energy of some of the surface electrons, ionisation occurs and the mol. will be adsorbed. (3) Adsorbed mols. will react as in the gaseous phase, but the energy of activation is lowered by ionisation or activation caused by the surface electrons and/or the number of active collisions between the mols. is increased. (4) New mols. having the highest ionisation energy and/or the lowest mol. wt. tend to be produced. (5) Rise of temp. increases

4 X

the number of collisions, but lowers the flow through the adsorption zone. (6) Pressure increases the flow through the adsorption zone. (7) The catalytic effect is proportional to the accessible area of the catalyst. The operation of these laws is demonstrated for the synthesis of NH_3, the decomp. of EtOH vapour, and the production of MeOH. The theory offers a simple explanation of many phenomena in which selective effects have hitherto been supposed. The theory is extended to enzymes, by assuming that an enzyme consists of mols. having electron-active groups (double linkings, C_6H_6 rings, etc.) adsorbed side by side on colloid surfaces, whereby mols. penetrating between the enzymic mols. are exposed to electronic impact.
E. S. HEDGES.

Catalytic decomposition of carbon monoxide. IV. Behaviour of nickel carbides. H. TUTIYA (Bull. Inst. Phys. Chem. Res. Tokyo, 1931, **10**, 951—973).—An X-ray investigation of the catalytic decomp. of CO by Ni or NiO has confirmed the formation of Ni_3C and a percarbide, Ni_2C. The percarbide is formed from NiO at 270° and rapidly decomposes into Ni_3C and C at 284°; it is also decomposed by atm. H_2O vapour. Ni_3C is quite stable at 285° and catalyses the decomp. of CO. In the temp. range of stability of Ni_3C the reaction $3Ni+2CO \rightleftharpoons Ni_3C+CO_2$ is possible, but not the reaction $2CO = C+CO_2$. Free Ni is found in the earlier stages of reduction of NiO, but later changes completely to carbides.
E. S. HEDGES.

Pressure hydrogenation with iodine as catalyst. J. VARGA and L. ALMÁSI.—See B., 1931, 1003.

Catalytic formation of methane from carbon monoxide and hydrogen. Simultaneous catalytic acceleration of the water-gas reaction and the Armstrong–Hilditch reaction. J. C. GHOSH, K. M. CHAKRABARTY, and J. B. BAKSHI (Z. Elektrochem., 1931, **37**, 775—779).—The reaction between CO and H_2 at 471° on a Ni–Th–Ce catalyst proceeds according to the equations $2mCO+2mH_2 \rightleftharpoons mCO_2+mCH_4$ and $nCO+nH_2+nH_2O \rightleftharpoons nCO_2+2nH_2$; no C separates. The ratio m/n diminishes with time, even with const. composition of the gas mixture, owing to the Ni losing its activity as regards CH_4 formation without, however, becoming less active as regards water-gas reaction. The mixture of reaction products has a higher heat of combustion than blue water-gas, viz., 426·5 B.Th.U. per cu. ft., and after removal of CO_2 and H_2O a higher val. than CO or carburetted water-gas, viz., 722 B.Th.U. per cu. ft. With one catalyst, at a gas velocity of 6500 c.c. per hr. per c.c. of catalyst, the equilibrium conditions of both the water-gas and the Armstrong–Hilditch reactions are attained at 471°.
H. F. GILLBE.

Catalytic decomposition of carbon disulphide by hydrogen. B. NEUMANN and E. ALTMANN (Z. Elektrochem., 1931, **37**, 766—771).—The reaction on a number of catalysts at 180—885° has been investigated. In all cases there is a max. in the temp.–% decomp. curve. The activity of the catalysts as regards the production of H_2S falls in the order Pt (90% decomp. at 500°), Cu, Pb, Cr oxide mixture, Ag, MgO+ThO (54% at 700°). The order is quite different if determined in terms of the total CS_2

decomposed, owing to the formation of other S compounds. Fractionation of the reaction products shows that the quantity of H_2S formed is very small at temp. below 600°, but rises rapidly thereafter to a max. at 850°; the amount of C_2H_4 produced falls to zero at about 700°, its place being taken by CH_4, of which the yield is a max. at 850°. The greater part of the H_2S produced results from the decomp. of org. compounds, and the usual simple formulation of the reaction is therefore incorrect. Although the equation $CS_2+4H_2=2H_2S+CH_4$ represents approx. the total reaction at 870°, the sequence of products at lower temp. is probably $CS_2 \rightarrow HCS_2H \rightarrow CH_2S \rightarrow MeSH \rightarrow CH_4$.
H. F. GILLBE.

Velocity of catalysed hydrogenation. I. A. KAILAN and (FRL.) H. C. HARDT (Monatsh., 1931, **58**, 307—368).—The hydrogenation velocities of cinnamic acid, its Me, Et, Pr^a, Bu^a, Ph, and CH_2Ph esters, oleic acid, and olive oil have been measured at 180—200° using Ni deposited by reduction on kieselguhr, or in some cases without carrier, as catalyst. In general, the unimol. velocity coeff. diminishes as the reaction proceeds, especially at the beginning, and experiments under apparently comparable conditions give very different results. The coeff. is least for the Et ester and greatest for the CH_2Ph ester. For the latter and for the Pr^a and Ph esters it is greater than for cinnamic acid itself. The coeff. for oleic acid is about the same as for cinnamic acid, but less for olive oil. The coeff. for olive oil increases rapidly as the reduction temp. of the catalyst rises from 250° to 320°, but much more slowly for higher reduction temp., especially above 460° (to 550°). Increase of the wt. of catalyst from 0·025 to 0·1 g. increases the velocity of hydrogenation of 20 g. of olive oil, but a further increase of the amount of catalyst to 2 g. produces no effect. If, instead of using 2 g. of kieselguhr containing 20% Ni, 0·4 g. of Ni alone is the catalyst, the coeff. is reduced 10—15 times, and it is always 0·2—0·25 as great if a Ni–kieselguhr prepared with Na_2CO_3 instead of NaOH is used, and 0·33—0·5 as great for a Ni–silicic acid catalyst. In the total hydrogenation of oleic acid more than 2H per mol. of acid is used. Experiments with stearic acid seem to indicate that this may be due to reaction with the CO_2H group.
M. S. BURR.

Catalytic reduction of carbon monoxide at the ordinary pressure. X. Influence of certain substances on the catalytic effect of Co–Cu–MgO. K. FUJIMURA (J. Soc. Chem. Ind., Japan, 1931, **34**, 384—386B, and Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **17**, 16—21).—The reduction of CO by H_2 in presence of Co–Cu–MgO is promoted considerably by the oxides of Th and U, and less by those of W, Mo, and Cr.
E. S. HEDGES.

Specificity of difficultly reducible oxide catalysts for hydrogenation. J. V. VAUGHEN and W. A. LAZIER (J. Amer. Chem. Soc., 1931, **53**, 3719—3728).—C_2H_4, C_3H_6, and C_4H_8, when mixed with H_2, are not hydrogenated by contact with Mo_2O_3, V_2O_3, MnO, MgO, TiO_2, ZnO alone or with Cr_2O_3, Al_2O_3, or Fe at 400°. Cu, Zn, and Zn on ZnO are effective. Hydrogenation of $COMe_2$ at 150 atm. with a ZnO–Cr_2O_3 catalyst affords 16% of $Pr^\beta OH$ with large recovery

of COMe₂. Na_2CO_3 on the catalyst prevents dehydration of $Pr^\beta OH$. It is suggested that in the oxide surface the valency forces of the metal atom are so strongly directed to the interior of the crystal lattice that weak negative groups (e.g., C:C) are not able to form a suitable complex with the surface to react with activated H_2. With such an oxide surface only COMe₂, $PhNO_2$, etc. can form an active complex.

J. G. A. GRIFFITHS.

Effect of phosphorus vapour on reaction between incandescent tungsten, water vapour, and oxygen, in presence of an inert gas. J. T. RANDALL and J. H. SHAYLOR (Trans. Faraday Soc., 1931, 27, 730—735).—Reactions in a gas-filled lamp are studied by the changing resistance of the filament. In absence of P, small quantities of H_2O give WO, whereas traces of O_2 give higher oxides; with P present, traces of H_2O do not attack the filament, but appear to give P_3O. C. W. DAVIES.

[Catalytic] conversion of methane. I, II. N. A. KLYUKVIN and S. S. KLYUKVINA (J. Chem. Ind., Russia, 1930, 7, 743—752, 877—885).—CH_4 was passed alone, and with CO_2 or H_2O, in presence of a catalyst, through heated porcelain or Fe tubes. With reduced NiO at 850° only 1·6% CH_4 remained unchanged; the gas contained H 94·3, N 4·1%, and the increase in vol. was 99·6%. The thermal decomp. of CH_4 may be complicated by formation of CO and CO_2 and (in absence of Ni) of unsaturated compounds. Equal vols. of CH_4 and CO_2 at 1000° with Ni gave 97·6% conversion: $CH_4 + CO_2 = 2CO + 2H_2$ (CO 47, H_2 48·6, N_2 2·6%); formation of CO begins at 700°. Addition of Al_2O_3 to Ni retards conversion. At 1000°, without a catalyst, 43% conversion occurred in a porcelain tube and 58% in a Fe tube. Under similar conditions the conversion of CH_4 is in direct proportion to the speed of the gas; the yield at 9 litres per hr. is 90% of that at 3 litres per hr. For the conversion $CH_4 + H_2O = CO + 3H_2$ (at low temp. $CH_4 + 2H_2O = CO_2 + 4H_2$; $CH_4 + CO_2 = 2CO + 2H_2$; $H_2O + CO = CO_2 + H_2$) the mixture of CH_4 with 4 vols. of steam was passed at a velocity of 6 litres per hr.; the best result gave 98·4% conversion of CH_4, with 218% increase in vol. (CO_2 5·8, CO 12·6, H_2 80, O_2 0·4, N_2 0·7, CH_4 0·5%). Substitution of Al_2O_3 or reduced Fe for Ni was unsatisfactory. Activated vegetable C gives 100% conversion (cf. Ni, 33·3%) at 800°; the conversion is accompanied by the reaction $C + 2H_2O = CO_2 + 2H_2$. Conversion of CH_4 with C in absence of H_2O gives 100% conversion at 900—950° (CO_2 0·2, CO 0·8, H_2 93·1, N_2 5·9%). With Ni the reaction of CH_4 alone starts at 300° and reaches complete conversion at 850°; with C it starts at 500—600°, and at 1000° 62·4% conversion takes place. Inactivated birch C gave 47·1% conversion of CH_4 at 1000° in a porcelain tube or 100% at 900° in a Fe tube. From 27 g. of C, 26·8 g. were recovered.

CHEMICAL ABSTRACTS.

Crystallised boron. L. HACKSPILL, A. STIEBER, and R. HOCART (Compt. rend., 1931, 193, 776—778). —A very condensed high-frequency spark is passed between electrodes of Mo or W in a mixture of H_2 and BCl_3 vapour. With 300 watts 0·5 g. of B is obtained in 3 hr. as a product of metallic appearance,

resembling As, hardness 9 (Mohs), d^{20} 3·33. It is attacked by aqua regia at 120—130°, and is at least 99% pure. X-Rays show it to be cryst., probably hexagonal. The product of the action of incandescent W on BBr_3 vapour is similar in structure, but not $B_{48}C_2Al_3$. C. A. SILBERRAD.

Separation of sulphide films on metals. E. BEUTEL and A. KUTZELNIGG (Monatsh., 1931, 58, 295—306).—Anodic separation of sulphide films of Au, Pt, and Pd from complex thiosulphate solutions and cathodic separation of the sulphides of Pb, Sb, Bi, Mn, Fe, Ni, and Co may be observed. When sol., the simple thiosulphate may be used. Cu_2S cannot be obtained electrolytically, but is formed by metallic contact. The anodic film usually contains free S and the cathodic film free metal. A covering layer of S is obtained on decomposing a Cu_2S or CoS film. The films were examined by micro-analytical methods. No sulphides were obtained with Ag, Zn, Cd, Hg, Sn, As, Mo, and U. M. S. BURR.

Preparation and some properties of amalgams of titanium, uranium, and vanadium. R. GROVES and A. S. RUSSELL (J.C.S., 1931, 2805—2814).—Conditions for depositing Ti, U, and V from aq. solution on a Hg cathode are given. The resulting amalgams have strong reducing properties, and the order of removal of the metals from Hg by oxidising solutions was determined (cf. A., 1929, 1402). The metals catalyse the production of H_2 at a Zn amalgam–dil. H_2SO_4 interface in the order (diminishing) Ti, U, V. Traces of each metal are deposited on Zn amalgam (also Ti and U on Sn and Cu amalgams and on Hg) on shaking solutions of the metal salts with the amalgams or Hg. H. J. EMELÉUS.

Electro-deposited metal foils. H. KERSTEN (Rev. Sci. Instr., 1931, [ii], 2, 649—653).—Electrolytic solutions are described for the deposition of Co, Ni, Cu, Ag, Cd, Sn, Au, and brass on polished stainless steel cathodes from which removal of the foil is easy. N. M. BLIGH.

Electrolytic preparation of β-tungsten. W. G. BURGERS and J. A. M. VAN LIEMPT (Rev. trav. chim., 1931, 50, 1050—1051).—Previous work (A., 1925, ii, 694) is incorrectly cited by other workers (this vol., 805). β-W (together with α-W) is formed when a mixture of K, Na, and Li tungstates is electrolysed at 500°. N. H. HARTSHORNE.

Anodic precipitation of lead peroxide. M. L. NICHOLS (Ind. Eng. Chem. [Anal.], 1931, 3, 384—385). —Experiments on the effect of rotation of the anode on the electrolysis of $Pb(NO_3)_2$ solutions indicate that the Pb is not carried to the anode in an ionic form, but is oxidised to negatively-charged PbO_2, which is then pressed against the anode by cataphoresis. This mechanism of formation of PbO_2 explains the difficulty of removing the last traces of H_2O in drying the deposit. E. S. HEDGES.

Electrolytic production of potassium ferricyanide. V. P. ILINSKI and N. P. LAPIN.—See B., 1931, 1047.

Behaviour of solutions of chlorine dioxide in carbon tetrachloride in the dark and in the light. R. LUTHER and R. HOFFMANN (Z. physikal. Chem.,

Bodenstein Festband, 1931, 755—769).—The partition coeff. at 17° of ClO_2 between CCl_4 and the gas phase is $50·7\pm0·4$, and between H_2O and the gas phase $34·3\pm0·1$. When ClO_2 is dissolved in CCl_4, Cl_2O is formed at a const. concentration of about $0·001M$, and causes in the dark further catalytic decomp. of the ClO_2. The active catalyst is probably ClO, and the kinetics of the reaction are represented fairly accurately by the equation $d[ClO_2]/dt = k[ClO_2]^{1\cdot3} . [Cl_2O]^{1\cdot3}$. By addition of alkali, preferably $Ba(OH)_2,8H_2O$, the decomp. is inhibited, but after several hr. have elapsed spontaneous decomp. commences. H. F. GILLBE.

Effect of light on formation of banded precipitates of mercuric iodide. R. TAFT and J. W. HILL (Trans. Kansas Acad. Sci., 1931, **33**, 57—63).—Light favoured the formation of the red form. The yellow form was transformed into the red (slowly in the dark) in silicic acid, but not in agar or gelatin. CHEMICAL ABSTRACTS.

Blackening of photographic plates by positive ions of the alkali metals. K. T. BAINBRIDGE (J. Franklin Inst., 1931, **212**, 489—506).—The energies, expressed in electron-volts, of the singly positively charged ions of the alkali metals required to produce a threshold opacity of $1·1$ on Eastman X-ray plates (the opacity being defined as the ratio of the light transmitted through the unexposed portion of the plate to that transmitted through the exposed portion) varied from 920 (Cs) to 460 (Li) for 1 min. exposure at a current density of $1·32\times10^{-8}$ amp. per sq. cm. For an opacity of 2 under the same conditions they varied from 1420 (Cs) to 860 (Li). The blackening at such low energies is only to a minor extent due to the penetration of the ions into the emulsion; impact radiation and the effect of electrons derived from the material of the apparatus play the larger part. The opacity is not proportional to the current density, and it is concluded that, regardless of the current density, only a limited no. of ions are effective in unit time. Eastman X-ray plates are about three times as sensitive to low-energy ions as Eastman process plates, but Schumann plates are more sensitive than either and will record K ions at 137 electron-volts under the above conditions. N. H. HARTSHORNE.

Significance of the redox [oxidation–reduction] potential of vat dyes for photographic and photochemical systems. A. STEIGMANN (Z. wiss. Phot., 1931, **30**, 69—76).—A discussion. Dyes which cause fogging of photographic emulsions act catalytically. In a given alkaline developer, the fogging is dependent on the potential of the dye, or the difference between that of the dye and of the reducing agent. In systems analogous to glutin–methylene-blue, exposure tends to increase such difference. As the difference increases, light-sensitivity increases, until the case of reduction in the dark is reached. J. LEWKOWITSCH.

Isolation of nuclei by developing agents. LÜPPO-CRAMER (Z. wiss. Phot., 1931, **30**, 65—68).—Metol, quinol, etc., in acidified KBr solution, partly remove the latent image; the more effective developers have the greater action. Development is considered

as the isolation of the latent image nuclei from adsorption on AgBr before chemical action occurs. J. LEWKOWITSCH.

Photochemical studies. II. C. WINTHER (Z. wiss. Phot., 1931, **30**, 113—120).—Actinometry using a solution of $(NH_4)_2C_2O_4$ and $HgCl_2$ is described. A brief review of photographic methods is given. J. LEWKOWITSCH.

Density surface of [a solid diagram representing] the Villard effect. H. ARENS and J. EGGERT (Z. wiss. Phot., 1931, **30**, 121—126).—After a const. exposure of a film to X-rays, the densities of the images produced by exposure to various light intensities for varying times have been measured. The results, showing the solarisation and fluctuation of density with const. val. of log it, are illustrated by a solid model, and also by density contour lines on a log i–log t graph. J. LEWKOWITSCH.

Solarisation. V. The latent image in the region of solarisation with physical development. H. ARENS (Z. wiss. Phot., 1931, **30**, 127—140; cf. B., 1931, 417).—The (a) grain wt., (b) grain no., and (c) amount of the latent image Ag have been determined using a special emulsion which shows solarisation with physical development. (a) and (c) increase steadily, from a low val., in the region of solarisation and second reversal; (b) decreases, following the developed Ag curve. The latent image becomes less sol. in Farmer's reducer in the solarisation region, probably owing to the smaller solubility of larger grains. If nitrite is added to the emulsion, all the characteristics increase steadily, (c) being exceptionally large, and solarisation is absent. Solarisation can be attributed to coagulation of Ag nuclei only if these are assumed to wander, since their mean separation is greater than their diameter. J. LEWKOWITSCH.

Photodichroism and photoanisotropy. IX. Photographic experiments with polarised light. I. F. WEIGERT and F. STIEBEL (Z. wiss. Phot., 1931, **30**, 95—107; cf. A., 1930, 519, 1238; this vol., 1250).—A chemical developer containing p-phenylenediamine is best for the production of photodichroism. Exposure of the plate to red polarised light with previous or subsequent exposure to red, or blue, ordinary light increases the dichroism greatly. The blue light can produce high vals. even when the exposure to polarised light is very small; in this case the effect is greater when the exposure to the blue light follows that to polarised light. J. LEWKOWITSCH.

Desensitisation [retardation of photolysis] in uranyl formate and potassium ferrioxalate. E. BAUR [with C. OUELLET and E. WÄCKERLIN] (Z. wiss. Phot., 1931, **30**, 88—94).—The rate of photolysis of uranyl formate in the presence of foreign substances has been measured and compared with the calc. figures (cf. A., 1929, 892). Experiments with $K_3Fe(C_2O_4)_3$, when the results are corrected to const. intensity of activating light, show a const. reaction velocity up to 30% decomp., in agreement with Allmand and Webb (*ibid.*, 1023). J. LEWKOWITSCH.

Photo-reduction of alcoholic solutions of ferric chloride. M. PRASAD and N. V. SOHONI (J. Indian

Chem. Soc., 1931, 8, 489—497).—The influence of the intensity of light, small amounts of H_2O, temp., and salts on the photo-reduction of solutions of $FeCl_3$ in anhyd. EtOH and n-amyl alcohol, and moist PrOH and BuOH has been studied. In conc. solutions the reaction is of almost zero order, but in dil. solution it becomes unimol., especially in presence of traces of H_2O; the order is partly governed by the light intensity. In anhyd. solutions a stationary state is attained, but addition of H_2O accelerates at first the reduction and then the back reaction. The temp. coeff. $(30—40°)$ is $1.00—1.15$. Traces of salts inhibit the reaction, and the effect increases with increase of the salt concentration.   H. F. GILLBE.

Products of photochemical oxidation of acetylene. R. LIVINGSTON (J. Amer. Chem. Soc., 1931, 53, 3909—3910).—$H_2C_2O_4$ and a trace of an aldehyde are formed when a mixture of C_2H_2 and O_2 saturated with H_2O vapour at room temp. is exposed in a flow system to the full radiation of the "hot" quartz Hg arc. The result is discussed in relation to the mechanism predicted by Mecke (this vol., 1136).
                                    J. G. A. GRIFFITHS.

Photolysis of diazo-compounds. I, II, III. I. FUKUSHIMA and M. HORIO (J. Soc. Chem. Ind., Japan, 1931, 34, 367—377B).—The decomp. of diazobenzenesulphonic acid (I) and of 1-diazo-β-naphthol-4-sulphonic acid (II) is influenced by light of wave-length shorter than 450 mμ and 380 mμ, respectively. The reactions proceed with const. velocity, independently of the concentration. The addition of quinine sulphate to a solution of the latter compound reduces the velocity of photolysis in proportion to the amount added. Rise of temp. has no influence on the photolysis of (II), but with (I) a thermal decomp. of the first order begins between $22°$ and $45°$.   E. S. HEDGES.

Photosynthetic activity of different catalysts. N. A. YAJNIK and F. C. TREHANA (J. Chim. phys., 1931, 28, 517—524).—Preliminary experiments confirm the results of Baly and co-workers (A., 1927, 1040). Blank experiments afford negligible org. residue. Several coloured solids suspended in H_2O were used as catalysts. With light from a 300-watt lamp, Cu arsenate afforded $0.129—0.174$ g. of org. residue containing 20 mg. of reducing substance (determined as dextrose); basic carbonates of Co and Ni, Cr phosphate, $CuCO_3$, and Cr_2O_3 afforded decreasing yields. $BaCrO_4$, Pb_3O_4, Fe_2O_3, and Ni phosphate afforded traces of org. residue but no reducing substances. Of $MgCO_3$, $BaSO_4$, $CaCO_3$, and MgO, alone, only $MgCO_3$ afforded a trace of org. substance, but when the first two were coloured with insol. dyes, org. reducing substances were obtained, the yields decreasing with change of colour from blue to red.   J. G. A. GRIFFITHS.

Action of high-speed cathode rays on simple alcohols, aldehydes, and ketones, and ethylene. J. C. MCLENNAN and W. L. PATRICK (Canad. J. Res., 1931, 5, 470—481).—Bombardment of the gaseous substances with high-speed cathode rays causes the following reactions. CH_2O gives paraformaldehyde, which decomposes into H_2, CH_4, and oxides of C. MeCHO and $COMe_2$ give gases and

polymerides; with MeCHO the reaction takes place on the wall of the vessel and the gases are formed by decomp. of the polymeride. MeOH and EtOH are primarily dehydrogenated to aldehydes, which then decompose. C_2H_4 yields a liquid, which gives H_2, C_2H_2, and saturated hydrocarbons on further bombardment. It is considered that clusters of mols. are first formed, which either (a) form solid or liquid condensates, or (b) decompose into simple gases.   R. S. CAHN.

Action of nitric oxide on alkaline hydroxides. E. BARNES (J.C.S., 1931, 2605—2620).—The reaction of the solid hydroxides of Li, Na, K, Rb, Cs, Ca, Sr, Ba with NO at 16—350° yields nitrites, N_2O, H_2O, and a small % of N_2, which increases with rise of temp. The reactivity of the alkali hydroxides increases with their mol. wts. The reaction of NO with 50% aq. KOH at $29.7°$ was approx. unimol., indicating a surface reaction or solution effect.
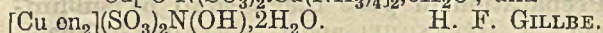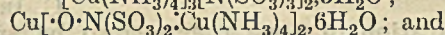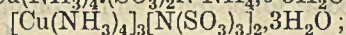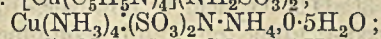   H. J. EMELÉUS.

Stability of potassium ferrocyanide solutions. I. M. KOLTHOFF and E. A. PEARSON (Ind. Eng. Chem. [Anal.], 1931, 3, 381—382).—$K_4Fe(CN)_6$ solutions should be kept in bottles of brown glass. The method of recrystallisation has no appreciable effect on the stability, but the presence of $K_3Fe(CN)_6$ tends to promote decomp.; dil. solutions are less stable than conc. solutions and the stability decreases with increasing acidity. Solutions containing 0.2% Na_2CO_3 are stable for long periods.   E. S. HEDGES.

Solid anhydrous copper hydride. E. PIETSCH and E. JOSEPHY (Naturwiss., 1931, 19, 737—738).—By the passage of at. H over Cu foil, a hydride is formed, appearing as a bluish-white film which gives reactions for $Cu^{··}$ and is very unstable in air.
                                    W. O. KERMACK.

Influence of substituents in the base and the anion on the co-ordination number of a metal. N. COSTĂCHESCU and A. ABLOV (Ann. Sci. Univ. Jassy, 1931, 16, 515—525).—The following compounds are described : $[Cu(C_5H_5N)_4](NH_2SO_3)_2$;
$Cu(NH_3)_4 ·(SO_3)_2N·NH_4, 0.5H_2O$;
$[Cu(NH_3)_4]_3[N(SO_3)_3]_2, 3H_2O$;
$Cu[·O·N(SO_3)_2·Cu(NH_3)_4]_2, 6H_2O$; and
$[Cu\ en_2](SO_3)_2N(OH), 2H_2O$.   H. F. GILLBE.

Reduction of silver chloride by sucrose and other reducing agents. E. V. ALEXEEVSKI and M. B. GOLDBERG (J. Gen. Chem. Russ., 1931, 1, 475—481).—AgCl is converted in alkaline solution into Ag_2O, which is reduced to Ag by sucrose, which is itself oxidised to CO_2, lævulic and formic acids. A similar reaction takes place using cellulose solutions in place of sucrose, but the velocity of reaction is considerably smaller. A suspension of AgCl in H_2O is only very slowly reduced by Zn dust; if, however, H_2O is added to an equimol. mixture of AgCl and Zn, reaction takes place with explosive violence, the production of a hard, porous conglomerate; this reaction does not take place if the mixture is added to H_2O. Mg, Al, and Fe do not react in the same way as Zn with AgCl, and Zn has no action on $Ag_4Fe(CN)_6$ or $Ag_3Fe(CN)_6$, whilst only a feeble reaction is observed with AgBr, AgI, and AgCNS.
                                    R. TRUSZKOWSKI.

Compounds of bi- and ter-valent silver.
G. A. BARBIERI (Atti R. Accad. Lincei, 1931, [vi],
13, 882—887).—Cd pyridine persulphate (A., 1911,
ii, 889) forms mixed crystals with Ag pyridine per-
sulphate and di-*o*-phenanthroline Cd persulphate with
the corresponding Ag compound (A., 1928, 1381).
The oxide Ag_2O_3, with the ratio active $O : Ag = 1.5 : 1$,
is obtained by hydrolysing either Ag peroxido-nitrate,
$AgNO_{11}$, or a HNO_3 solution of AgO.
                         T. H. POPE.

Ammines of complex thiocyanates. G. SPACU
and G. GRECU (Bul. Soc. Stiinte Cluj, 1931, **5**, 422—
440; Chem. Zentr., 1931, i, 3342).—The following
compounds have been prepared : $[Ag(SCN)_3][Cu \ en_2]$,
$[Ag(SCN)_3][Ni \ en_2]$, $[Zn(SCN)_4][Cu \ en_2]$,
$[Zn(SCN)_4][Zn \ en_2]$, $[Cd(SCN)_4][Cd \ en_2]$,
$[Hg(SCN)_4][Cu \ en_2]$, $[Hg(SCN)_4][Ni \ en_2]$,
$[Hg(SCN)_4][Zn \ en]$, $[Hg(SCN)_4][Zn \ en_2]$,
$[Hg(SCN)_4][Hg \ en_2]$, $[Hg(SCN)_4]_3[CO \ en_3]_2$,
$[Ni(SCN)_6][Ni \ en_2]_2$, $[Cr(SCN)_6][Cu \ en_2]_3$,
$[Cr(SCN)_6]_2[Cd \ en_3]_3$. SCN has a greater tendency
than I to form complexes. The stability of com-
plexes diminishes in the order CN, F, SCN.
                       A. A. ELDRIDGE.

Solid gold hydride. E. PIETSCH and E. JOSEPHY
(Naturwiss., 1931, **19**, 737).—By the passage of at.
H over pure Au foil, a Au hydride is formed which
appears as a whitish film on the surface of the
foil. The hydride is stable only for a short time in
the air or in H_2, and is decomposed at 100°. It gives
reactions indicating the presence of Au ions.
                       W. O. KERMACK.

**Hydrothermal synthesis of calcium silicates
with pressure. II.** S. NAGAI (J. Soc. Chem. Ind.,
Japan, 1931, **34**, 317—319B).—At 153° and 5 kg. per
sq. cm. combination is very slow, the product being
a hydrate of $3CaO,2SiO_2$. At 181° and 10 kg. per
sq. cm. the above compound is the first product, but
longer heating or an excess of SiO_2 yields CaO,SiO_2.
If SiO_2 is present in great excess CaO,SiO_2 is formed
first, but heating at 211°/20 kg. per sq. cm. produces a
hydrate of $3CaO,2SiO_2$, which, however, differs from
that produced at lower temp. in its combined H_2O.
                       C. IRWIN.

**Preparation of pure magnesium by sublim-
ation.** J. HÉRENGUEL and G. CHAUDRON (Compt.
rend., 1931, **193**, 771—773).—The apparatus is made
of steel calorised on its inner surface, with water-
cooled joints made staunch with rubber, and means
for filling it with A. A vac. of 0·01 mm. is main-
tained. Mg then sublimes without melting at 600°
at the rate of 1 kg. per hr. Si remains as $SiMg_2$; Cl,
Na, and C appear in the upper part of the condenser
as $MgCl_2$, Na and its carbide. The sublimed Mg con-
tains 0·001% Cl, <0·001% Si, and <0·01% Fe;
resublimed, only <0·001% Cl. It forms large den-
drites, which must be melted in A.
                       C. A. SILBERRAD.

Alumino-oxalates. G. J. BURROWS and K. H.
LAUDER (J. Amer. Chem. Soc., 1931, **53**, 3600—3603).
—*Aluminium trioxalic acid*, $H_3Al[(C_2O_4)_3]$,9EtOH, is
prepared by warming $Al(OEt)_3$ with $H_2C_2O_4$ in abs.
EtOH. The Na_3 (+2EtOH), trianiline, *dl*-, *d*-, and
l-strychnine, and *d*- and *l*-K_3 salts have been prepared
and described (cf. A., 1927, 339). Fractional crystall-

isation of the *dl*-strychnine salt from a EtOH–$CHCl_3$
mixture affords the *l*-salt. The isomerides racemise
rapidly. $H_3Al[(C_2O_4)_3]$,9EtOH kept over H_2SO_4 in
vac. for many weeks affords $H[Al(C_2O_4)_2]$,4EtOH when
recryst. from abs. EtOH. In this *acid* and the Na
salt (+EtOH), Al has a co-ordination valency 4.
$Na_2[Al(C_2O_4)_2OHOH_2]$,H_2O and the Ba salt (+H_2O)
have been prepared.   J. G. A. GRIFFITHS.

**Affinity. LIV. Constitution of compounds
of aluminium halides with ammonia. I.** W.
KLEMM and E. TANKE. **LV. II. Monoammines as
molecular additive compounds.** W. KLEMM, E.
CLAUSEN, and H. JACOBI (Z. anorg. Chem., 1931, **200**,
343—366, 367—384; cf. Haraldsen and Biltz, this
vol., 1128).—LIV. Tensimetric and thermal measure-
ments have shown the existence of the following
compounds in addition to those previously established :
$AlCl_3$ with 1, 7, 14; $AlBr_3$ with 1, 3 (probably), 5, 7,
9, 14; AlI_3 with 1, 3 and 5 probably, 7, 9, 13 mols.
NH_3. Densities, heats of formation, and m. p. of
the lower members have been determined. The three
monoammines have the same m. p. (125°±3°), and,
unlike the parent salts, probably possess the same
structure. The ammines of the Al halides and of
the In halides are analogous. The properties of the
Al ammine halides are compared with those of some
closely related compounds.
     LV. Electrical conductivities and mol. vols. of the
monoammines have been determined. The chloride
and bromide compounds are unimol. in the state of
vapour. All the experimental evidence indicates that
the character of the mol. is represented by the formula
$[AlX_3,NH_3]$. A model is given.   F. L. USHER.

Structure of ultramarine. K. LESCHEWSKI and
H. MÖLLER (Naturwiss., 1931, **19**, 771—772).—Molten
HCO_2Na and blue ultramarine, when heated at 350—
400°, give a colourless compound, which turns green
when washed with H_2O. The green colour disappears
with further washing, and the resulting white sub-
stance is a true ultramarine, which can be converted
by dry heat into blue ultramarine. The white ultra-
marine is a reduction product of the blue variety.
Blue ultramarine yields, on prolonged boiling with
ethylene chloride, a rose-coloured ultramarine, which
on dry heating is converted into blue with the emission
of mercaptan-like odours. White ultramarine can
be prepared by the decomp. of blue ultramarine by
dry gaseous HCl in high-boiling alcohols (*e.g.*, glycol,
glycerol). When heated, this substance turns olive-
brown, assuming a grey colour on cooling. On
sulphurisation this substance reverts to the original
blue colour.   W. R. ANGUS.

Amphoteric nature of aluminium hydroxide.
R. A. ROBINSON and H. T. S. BRITTON (J.C.S., 1931,
2817—2820).—The conductometric titration of
0·003125M-$Al_2(SO_4)_3$ with 0·2N-NaOH and the back-
titration with 0·2N-HCl indicated the following
reactions : $Al_2O_3,3SO_3 \longrightarrow Al_2O_3,2\cdot68SO_3$ (sol.)$\longrightarrow$
$Al_2O_3,0\cdot6SO_3$ (insol.)$\longrightarrow Al_2O_3,0\cdot12SO_3$ (max. insol.)
$\longrightarrow NaAlO_2$. The equiv. conductivity of $NaAlO_2$ was
approx. 60.   H. J. EMELÉUS.

Sulphides of rare-earth metals. PICON and
COGNÉ (Compt. rend., 1931, **193**, 595—597).—By the

method used in preparing Ce_2S_3 (cf. this vol., 582) pure Y_2S_3, La_2S_3, Nd_2S_3, and Sm_2S_3 have been obtained as vitreous masses, transparent in thin sections, coloured (in the above order) citron-yellow, yellowish-white, greenish-yellow, and rose-yellow; d 3·910, 4·997, 5·387, and 5·729; m. p. (vac.) 1900—1950°, 2100—2150°, 2200°, and 1900°. Volatilisation begins at 1900°, 1900°, 2100°, and 1800°. Although H_2, N_2, and CO are without action at fairly high temp., by heating in H_2 for 30 min. at 2700° the losses of Y_2S_3, La_2S_3, Ce_2S_3, Nd_2S_3, and Sm_2S_3 are respectively 35, 30, 28, 30, and 82%, the residues of Y_2S_3 and Sm_2S_3 being carburised and containing 3% S; of La_2S_3, Ce_2S_3, and Nd_2S_3 slightly carburised and containing 16, 12, and 12% S, respectively. Losses in N_2 at 2800° are recorded. Stability, save in the case of Sm, increases with at. wt.　　　C. A. SILBERRAD.

Separation of rare earths by fractional crystallisation. S. FREED (J. Amer. Chem. Soc., 1931, **53**, 3906—3907).—Utilisation of the differences of ionic radii in the separation of rare earths should be possible with unsolvated ions and crystallisation at low temp.
J. G. A. GRIFFITHS.

Praseodymium and thallous sulphates. F. ZAMBONINI and S. RESTAINO (Atti R. Accad. Lincei, 1931, [vi], **13**, 650—654).—The system $Pr_2(SO_4)_3$–Tl_2SO_4–H_2O has been studied at 25°. Four compounds are formed, viz., $Pr_2(SO_4)_3,5Tl_2SO_4$, $Pr_2(SO_4)_3,4·5Tl_2SO_4$, $Pr_2(SO_4)_3,3Tl_2SO_4,H_2O$, and $Pr_2(SO_4)_3,Tl_2SO_4,4H_2O$. Slow evaporation at a temp. not higher than 12—13° of a solution containing the two sulphates in any proportions yields $Pr_2(SO_4)_3,Tl_2SO_4,8H_2O$. The crystallography of the octo- and tetra-hydrates is discussed.
H. F. GILLBE.

Permutoid reactions of graphite. U. HOFMANN and A. FRENZEL (Z. Elektrochem., 1931, **37**, 613—618).—Graphite is transformed by H_2SO_4–HNO_3 mixtures into a bluish form, which slowly reverts to the initial form. X-Ray spectrograms indicate an increase in the distance between the planes of the C atoms. The swelling of graphitic acid in H_2O can be followed in the same way. By gently heating graphite acid in vac., oxides of C are lost and the residue consists of graphite. X-Ray spectrographic examination of this change indicates that graphitic acid is a surface compound in the Langmuir sense. E. S. HEDGES.

Pneumatolytic synthesis of silicates. II. C. J. VAN NIEUWENBURG and H. B. BLUMENDAL (Rec. trav. chim., 1931, **50**, 989—996; cf. this vol., 322).—SiO_2 volatilised in supercrit. steam reacts with CdO to give Cd_2SiO_4, with kaliophilite to give leucite and orthoclase, and with nephelite to give analcite and albite, this difference in the behaviour of the K and Na compounds being in accord with the results of many hydrothermal syntheses and with geological evidence. Preliminary experiments indicate that the presence of CO_2 in such reactions markedly inhibits the formation of silicates. TiO_2 and SnO_2 do not volatilise in supercrit. steam, but MoO_3 and WO_3 do so, and in this condition react with CaO to give $CaMoO_4$ and $CaWO_4$. Cu may also be so volatilised.
N. H. HARTSHORNE.

Copper, cobalt, nickel, zinc, and cadmium tetrapyridine fluosilicates. W. T. L. TEN BROECK, jun. [with P. A. VAN DER MEULEN] (J. Amer. Chem. Soc., 1931, **53**, 3596—3600).—The addition of pyridine to aq. solutions of metallic fluosilicates affords the following complex *salts* : $Cu(C_5H_5N)_4SiF_4,H_2O$ and $X(C_5H_5N)_4SiF_6$, where X=Co, Ni, Zn, and Cd. The dissociation pressures when the Co salt loses 1 and 2 mols. of pyridine have been determined between 35° and 83°; at higher temp. SiF_4 is evolved. At sufficiently high temp. the other salts yield pyridine together with SiF_4.　　　J. G. A. GRIFFITHS.

Cerium, lanthanum, praseodymium, and neodymium mercurides. P. T. DANILTSCHENKO (J. Gen. Chem. Russ., 1931, **1**, 467—474).—The alloy obtained by fusing together CeO_2, Mg, and Hg contains up to 5% Mg, which can be removed by repeated extraction with hot, very dil. HCl. The product, on distillation under reduced pressure in the absence of O_2, loses Hg, to yield a cryst. residue of $CeHg_4$, which above 470° is converted into $CeHg_3$. $LaHg_4$, $NdHg_4$, and $PrHg_4$ are prepared in the same way as $CeHg_4$, and possess similar properties. R. TRUSZKOWSKI.

Arsenic tri-iodide. W. H. MADSON and C. KRAUSKOPF (Rec. trav. chim., 1931, **50**, 1005—1010).—AsI_3 (99·81% pure), m. p. 138·6°, was prepared by a modification of Oddo and Giachery's method (A., 1923, ii, 316), the product being extracted with mustard oil and recryst. from CS_2. In air it decomposes very slowly below 100°, slowly at 137°, and rapidly at 200°, giving I, As_2O_3, and As. In N_2 it decomposes above 100°. Solutions in a large number of common org. solvents all showed decomp. which was accelerated by H_2O and O_2, but not by light.　　　N. H. HARTSHORNE.

Form of separation of sulphur. H. TOMINAGA (J. Fac. Sci. Hokkaido, 1931, **1**, 181—183).—The reaction between NO and H_2S was investigated between 12° and 50°. The S produced was brown and transparent in the initial stages (labile liquid form) until the point of min. pressure was reached, when it became pale yellow and turbid (stable cryst. form).
P. G. MARSHALL.

Thermal behaviour of sulphur compounds in hydrocarbon solvents. I. **Aliphatic mercaptans.** W. M. MALISOFF and E. M. MARKS.—See this vol., 1393.

Process of decomposing chromite. II. **Compounds of chromic sulphate with sulphuric acid alone and with sulphates of bivalent metals.** Y. KATO and R. IKENO (J. Soc. Chem. Ind., Japan, 1931, **34**, 311—312B; cf. B., 1930, 903).—If $Cr_2(SO_4)_3$ is boiled with H_2SO_4 there is formed at 250° $Cr_2(SO_4)_3,H_2SO_4$, and this salt is decomposed at 280°. Both the acid salt and the anhyd. sulphate are almost insol. in H_2O. A series of compounds or solid solutions, also almost insol., is formed by boiling $Cr_2(SO_4)_3$ and H_2SO_4 with sulphates of Cu, Zn, Co, Cd, Mg, Fe··, and Mn··.　　　C. IRWIN.

Amminochromic carbonates. J. BANCELIN (Compt. rend., 1931, **193**, 597—598).—By the action of ammoniacal $(NH_4)_2CO_3$ on anhyd. $CrCl_2$ a yellow insol. ppt. is formed of $[Cr(NH_3)_2(H_2O)_4]_2(CO_3)_3$, stable

in presence of NH_3, but in air soon turning greyish-violet; if washed and dried in H_2 it can be preserved in a sealed tube. Cold dil. HCl affords a green solution yielding on evaporation green $[Cr(NH_3)_2(H_2O)_4]Cl_3$ (cf. A., 1902, ii, 210). The change to the greyish-violet compound, although rapid at first, takes long to complete. The formula $[Cr_3(NH_3)_2(H_2O)_9(OH)_3(CO_3)_2](OH)_2$ is proposed.
C. A. SILBERRAD.

Fourth degree of oxidation of molybdenum. W. F. JAKÓB and E. TURKIEWICZ (Rocz. Chem., 1931, **11**, 569—576).—In the prep. of $K_4Mo(OH)_4(CN)_4$ from KCN and $MoO(OH)_3$ Mo^V is converted into Mo^{IV} and Mo^{VI}, which alone combines with KCN. The reaction proceeds according to the equations:

$$(OH)_4Mo \cdot O \cdot MoO(OH)_2 + 2OH' \rightleftharpoons$$
$$[(OH)_4Mo \cdot O \cdot MoO_3]'' + 2H_2O, \text{ and}$$
$$[(OH)_4Mo \cdot O \cdot MoO_3]'' \rightleftharpoons$$
$$\xrightarrow{+4CN'}$$
$$[(OH)_4Mo^{IV} - - - O \vdots Mo^{VI}O_3]'' \rightleftharpoons$$

$[Mo^{IV}(CN)_4(OH)_4]'''' + MoO_4''$. $K_4[Mo(CN)_4(OH)_4]$ is converted into octocyanide on keeping in solution with excess of CN and H ions. R. TRUSZKOWSKI.

Tungsten oxytetrachloride. W. REINDERS and J. A. M. VAN LIEMPT (Rec. trav. chim., 1931, **50**, 997—1003).—$WOCl_4$ is best prepared by passing Cl_2 over an equimol. mixture of W and WO_2, followed by distillation in vac., or in a stream of CO_2 at 200—210°. The product has m. p. 209°, b. p. 233°, heat of sublimation 18,284, heat of vaporisation 16,840 g.-cal. per mol. N. H. HARTSHORNE.

Heteropolycyclic compounds. I. Sodium salts of phosphotungstic acid. II. Sodium phosphomolybdate. A. V. RAKOVSKI and E. A. NIKITINA (J. Gen. Chem. Russ., 1931, **1**, 240—246, 247—252).—I. The optimum method for the prep. of Na phosphotungstate is the condensation of Na_2HPO_4 and Na_2WO_4 by the action of HCl. Recrystallisation from alkaline solution gives $Na_3H_4[P(W_2O_7)_6], nH_2O$, or from acid solution $Na_2H_5[P(W_2O_7)_6], nH_2O$. Quinoline acetate is recommended as a precipitant of tungstic and phosphotungstic acids.

II. The action of H_3PO_4 on Na paramolybdate gives yellow compounds, but on evaporation only Na phosphate and molybdate are obtained. The action of MoO_3 on Na_2HPO_4 gives $Na_4H_8[P_2O_2(Mo_2O_7)_9], nH_2O$. A method is described for the prep. of the trisubstituted salt $Na_3H_7[P(Mo_2O_7)_2], nH_2O$, which also gives the disubstituted salts in strongly acid solutions. The salt decomposes readily. E. B. UVAROV.

Ammines of uranium. R. RĂSCANU (Ann. Sci. Univ. Jassy, 1930, **16**, 32—56, 459—496).—The prep. and properties of the following compounds with pyridine, quinoline, 2-methylquinoline, antipyrine (Ap), pyramidon (Pm), and phenacetin (Pn) are described:
$[UO_2,C_5H_5N](NO_3)_2$; $[UO_2,C_5H_5N,H_2O](NO_3)_2$; $[UO_2,C_9H_7N,H_2O](NO_3)_2$; $[UO_2,C_{10}H_9N,H_2O](NO_3)_2$; $[UO_2,Ap_2](NO_3)_2$; $[UO_2,Ap_2]Cl_2$; $[UO_2,Ap_2]Br_2$; $[UO_2,Ap_2]SO_4,4H_2O$; $[UO_2,Pm_2](NO_3)_2$; $[UO_2(C_5H_5N)_2]Cl_2$; $[UO_2,Pm_2](NO_3)_2$ (dark red and light red forms); $[UO_2,Pm_2]Cl_2$;

$[UO_2,Pm_2,H_2O]Cl_2,H_2O$; $[UO_2,Pm,H_2O]Cl_2$; $[UO_2,Pm,H_2O]Cl_2,2H_2O$; $[UO_2,Pm]Cl_2$; $[UO_2,Ap_2](OAc)_2$; $[UO_2,Ap,H_2O]C_2O_4$; $[UO_2,Pn_2](NO_3)_2$; $[UO_2,Pn_2]Cl_2$; $[UO_2,Pn_2(H_2O)_2]Cl_2$; $[UO_2,Pn_2(H_2O)_3]Cl_2$; $[UO_2,Pn_2(H_2O)_2]Cl_2,2H_2O$; $[UO_2,Pn_3]Cl_2$; $[UO_2,Pn,2H_2O]C_2O_4$; $[UO_2,Pn_4]Br_2$; $[UO_2,Pn_4(H_2O)_7]Br_2$. H. F. GILLBE.

Rhenium. III. Compounds of ter- and quadri-valent rhenium. F. KRAUSS and H. STEINFELD (Ber., 1931, **64**, [B], 2552—2556; cf. this vol., 53).—Treatment of a mixture of $KReO_4$ and KI with HCl (d 1·18) and immediate boiling until evolution of I ceases affords the *salt* $K_3[ReCl_6]$, decomposed by a large excess of H_2O at room temp. (corresponding Tl_3 *salt*). Under somewhat different conditions the *compound* $K_4Re_2Cl_{11}$ (? $K_2[ReCl_5] + K_2[ReCl_6]$) is produced (corresponding Tl_4 *salt*). $KReO_4$, KBr, and conc. HBr give the *compound* $K_2[ReBr_6]$, whilst the *salt* $Tl_2[ReBr_6]$ is obtained from $TlReO_4$ and HBr (d 1·75).
H. WREN.

Nitrosothio-salts of iron: nitrosodithiocarbamates. L. CAMBI and A. CAGNASSO [with A. TANARA] (Atti R. Accad. Lincei, 1931, [vi], **13**, 254—257; cf. this vol., 934).—The prep. of the *dithiocarbamates* $[Me_2N \cdot CS_2]_3Fe$ and $[C_5H_{10}N \cdot CS_2]_3Fe$ is described. They are very similar to the ferric xanthates, but are stable towards atm. O_2 and towards NO. The ferrous salts, however, react with NO and form the *nitrosodithiocarbamates* $[Me_2N \cdot CS_2]_2Fe \cdot NO$ and $[C_5H_{10}N \cdot CS_2]_2Fe \cdot NO$.
O. J. WALKER.

Rôle of hydrogen in the dissolution of iron. H. CASSEL and T. ERDEY-GRÚZ (Z. physikal. Chem., 1931, **156**, 317—318).—An explanation alternative to that proposed by Liebreich (cf. this vol., 1016) is put forward. F. L. USHER.

[**Rôle of hydrogen in the dissolution of iron.**] E. LIEBREICH (Z. physikal. Chem., 1931, **156**, 319—320).—A reply (see preceding abstract).
F. L. USHER.

Hexacyanocobaltic acid and ethyl alcohol. F. HÖLZL [with G. SCHINKO] (Monatsh., 1931, **58**, 249—267; cf. this vol., 944).—By passing gaseous HCl into a solution of $H_3[Co(CN)_6]$ in abs. EtOH, a cryst. ppt. of $H_3[Co(CN)_6],3EtOH$, or more probably the oxonium compound $[Co(CN)_6](EtOH \cdot H)_3$, is formed. This compound is also in stable equilibrium with a saturated solution of $H_3[Co(CN)_6]$ in abs. EtOH between 0° and 75°. Tensimetric measurements indicate that, under diminishing pressure, EtOH is removed in successive stages, with the formation of intermediate additive compounds until the free acid is left. The process is facilitated by rise in temp. On keeping the EtOH solution at higher temp. (78° and 98°) the acidity to phenolphthalein diminishes. In the absence of H_2O an amount of EtNC, equiv. to the change in acidity, is formed. The presence of H_2O results in side reactions with the formation of HCN. According to the conditions of temp. and H_2O content a number of different *compounds* may be formed: with abs. EtOH,
$[(CN)_2(H_2O)_2Co \vdots (CN)_2 \vdots Co(CN)_2(EtNC)(H_2O)]$ and

$[(CN)(H_2O)_2Co:(CN)_3:Co(CN)_2(EtNC)]$; with 96% EtOH $[(H_2O)_3(CN)_2Co \cdot (CN) \cdot \{Co(CN)_4\} \cdot (CN) \cdot Co(CN)_2 (EtNC)]H$ and $(OH)_2[(H_2O)_2(CN)_2Co:(CN)_2 \cdot \{Co(CN)_4\}: (CN)_2:Co(CN)_2(H_2O)(EtNC)]H$; with 90% EtOH, $[(H_2O)_3(CN)_2Co \cdot CN \cdot \{Co(CN)_4\} \cdot CN \cdot \{Co(CN)_4\} \cdot (CN) \cdot Co(CN)_2(H_2O)_3]H_3$; and with 80% EtOH, $[(CN)_2(H_2O)_2 Co:(CN)_2 \cdot \{Co(CN)_2\}:(CN)_2:Co(CN)_2(H_2O)_2]$ and $[(CN)_3 (H_2O)Co:(CN)_2 \cdot \{Co(CN)(H_2O)\}:(CN)_2 \cdot \{Co(CN)(H_2O)\}: (CN)_2:Co(CN)_2(H_2O)_2]H$. M. S. BURR.

Complex nickel salts. J. DALIETOS (Praktika, 1931, **3**, 754—760; Chem. Zentr., 1931, i, 3445—3446).—The salts $[Ni\ en]SO_4,2H_2O$, $[Ni\ en]Cl_2$, $[Ni\ en]Br_2$, $[Ni\ en](NO_3)_2$, and $[Ni(C_5H_5N)]SO_4$ were prepared. A. A. ELDRIDGE.

Complex ruthenium compounds. R. CHARONNAT (Ann. Chim., 1931, [x], **16**, 123—250; cf. this vol., 1256).—$K\ Ru^{III}\ oxalate$, $2K_3Ru(C_2O_4)_3,9H_2O$, and the corresponding NH_4 and Na salts, $(NH_4)_3Ru(C_2O_4)_3,3H_2O$ and $Na_3Ru(C_2O_4)_3,5H_2O$, have been prepared by interaction of the alkali oxalates with the corresponding chlororuthenates or $RuCl_4$. The mixed compounds $Na_{19}K_5[Ru(C_2O_4)_3]_8,32H_2O$, $(Ag,K)_3Ru(C_2O_4)_3,3H_2O$, and $BaKRu(C_2O_4)_3,3H_2O$ have been obtained similarly. The double salts $2K_3Ru(C_2O_4)_3,KCl,8H_2O$ and $2K_3Ir(C_2O_4)_3,Hg(CN)_2,8H_2O$ have been prepared. Compounds with strychnine, $KH_2Ru(C_2O_4)_3,2C_{21}H_{22}O_2N_2,4H_2O$ and $H_3Ru(C_2O_4)_3,3C_{21}H_{22}O_2N_2,12H_2O$, have been obtained. The compound $K_3RuCl_2(C_2O_4)_2,H_2O$ is an intermediate product in the formation of $K_3Ru(C_2O_4)_3$. On oxidation in aq. solution the latter compound passes into $K_2Ru(C_2O_4)_3$; from which the strychnine compound $H_2Ru(C_2O_4)_3,2C_{21}H_{22}O_2N_2,8H_2O$ may be obtained, and forms with pyridine the compounds $K(C_5H_5N)_2Ru(C_2O_4)_2,6H_2O$ and $K(C_5H_5N)_2Ru(C_2O_4)_2,2H_2O$. $K\ Ru^{IV}\ nitrosochlorodi-oxalate$, $K_2Ru(NO)Cl(C_2O_4)_2,H_2O$, is formed by the action of $K_2C_2O_4$ on $K_2Ru(NO)Cl_5$, whereas with $K_2Ru(NO)I_5$ a similar I compound, $K_2Ru(NO)I_3(C_2O_4),H_2O$, results. The following mono-pyridinenitrosodioxalate derivatives of Ru^{IV} have been obtained : $2KRu(NO)(C_5H_5N)(C_2O_4)_2,9H_2O$, $AgRu(NO)(C_5H_5N)(C_2O_4)_2$, and $Ba[Ru(NO)(C_5H_5N)(C_2O_4)_2]_2$. The corresponding compounds with l-quinine, d-quinidine, NH_4, and C_5H_5N, $HRu(NO)(C_5H_5N)(C_2O_4)_2,C_{20}H_{24}O_2N_2,H_2O$, $HRu(NO)(C_5H_5N)(C_2O_4)_2,C_{20}H_{24}O_2N_2,H_2O$, $NH_4Ru(NO)(C_5H_5N)(C_2O_4)_2,H_2O$, and $HRu(NO)(C_5H_5N)(C_2O_4)_2,C_5H_5N$, respectively, each have been isolated in two forms, corresponding with the d- and l-forms of the $Ru(NO)(C_5H_5N)(C_2O_4)_2$ ion, the mol. rotation of which is about 2400°. By the action of HCl on $KRu(NO)(C_5H_5N)(C_2O_4)_2$ there is formed $K\ Ru^{IV}\ nitrosopyridine\ tetrachloride$, $KRu(NO)(C_5H_5N)Cl_4$. Interaction of pyridine with $K_2Ru(NO)Cl(C_2O_4)_2$ gives $dipyridine\ Ru^{IV}\ nitroso-chloro-oxalate$, $(C_5H_5N)_2Ru(NO)Cl(C_2O_4)$, which yields $dipyridine\ Ru^{IV}\ nitrosotrichloride$, $(C_5H_5N)_2Ru(NO)Cl_3,3H_2O$, on addition of HCl, and by hydrolysis of this compound $dipyridine\ Ru^{IV}\ nitroso-hydroxydichloride$, $(C_5H_5N)_2Ru(NO)(OH)Cl_2$, results. By interaction of $K_2Ru(NO)Cl_5$ with $C_2H_4(NH_2)_2$ and

NaI there is formed the compound $Ru(NO)I_3,en$, then the compound $[Ru(NO)(OH)\ en_2]I_2$. The compounds $[Ru(NO)(OH)\ en\ (NH_3)_2]I_2$ and $[Ru(NO)(OH)\ en\ (C_5H_5N)_2]I_2$ are obtained from $Ru(NO)I_3,en$. By the action of HCl, HBr, and HI on $[Ru(NO)(OH)\ en_2]I_2$ the compounds $[Ru(NO)(Cl,H_2O)\ en_2]I_2$, $[Ru(NO)Br\ en_2]I_2$, and $[Ru(NO)I\ en_2]I_2$, respectively, are obtained. The compounds $[Ru(NO)Br\ en_2]Br_2$, $[Ru(NO)I\ en_2]Br_2$, and $[Ru(NO)(Cl,H_2O)\ en_2]Cl_2$ have also been prepared. The compound $[Ru(NO)I\ en_2]I_2$ exists in two isomeric forms. It appears probable that in some of the above compounds the co-ordination no. of Ru is 8. R. CUTHILL.

Promoters of crystallisation in micro-chemistry. F. AMELINK (Pharm. Weekblad, 1931, **68**, 1086—1088).—A review of methods suitable for micro-reactions. Various examples are given of the method in which a trace of the anticipated ppt. is added to one of the reactants. H. F. GILLBE.

Heyrovsky's electroanalytical polarographic methods and their applications in theoretical and practical chemistry. W. KEMULA (Z. Elektrochem., 1931, **37**, 779—795).—A full account of the theory and practice of the method, with an extensive bibliography. H. F. GILLBE.

Tetramethyldiaminodiphenylmethane [as analytical reagent]. J. B. FICKLEN (Chem. and Ind., 1931, 869).—It is suggested that $CH_2(CH_4 \cdot NMe_2)_2$ could be used to detect small quantities of many elements which have at least two relatively stable valency forms and have a higher oxide or hydroxide which are insol. in the oxidising solution. In using the reagent (cf. Harry, this vol., 1385) it is necessary to eliminate or correct for other reacting materials. E. S. HEDGES.

Indicators. XVIII. "Hydrogen effect" and salt error of indicators. A. THIEL and G. COCH (Z. anorg. Chem., 1931, **200**, 419—428; cf. A., 1929, 1410).—Potentiometric determination of the p_H of phosphate buffer solutions in presence of NaCl or KCl, and colorimetric examination of the same solutions when containing various indicators, point to the non-existence of a "H effect" as defined by Wolf (A., 1930, 1391). The effect observed in weakly buffered solutions is due to contamination with traces of CO_2. The potentiometric method is free from objection when proper precautions are observed. F. L. USHER.

Continuous measurement of p_H with quin-hydrone electrodes. C. C. COONS (Ind. Eng. Chem. [Anal.], 1931, **3**, 402—407).—The concentration of quinhydrone necessary for measurements with an accuracy of $\pm 0.05\ p_H$ is 7 mg. per 100 c.c. of solution. A method for determining the concentration of quinhydrone dissolved in H_2O is outlined and the solubility curve for quinhydrone is given from 0° to 50°. The practicability of various methods of adding quinhydrone to a flowing solution for the purpose of obtaining continuous p_H measurements is discussed, and the continuous addition of a solution of quin-hydrone from an external source is considered to be best. Pt electrodes are better than Au electrodes

for continuous p_H measurement; they should be cleaned by washing in boiling 5—10% $NaHSO_3$ solution.   E. S. HEDGES.

Modified absorption tube for determination of hydrogen in organic substances by the micro-analytical method of Pregl. W. J. BOYD and W. ROBSON (J.S.C.I., 1931, 50, 400—402T).—The adoption of P_2O_5 as absorbent for H_2O in the Pregl process permits the use of an absorption tube which weighs 1·5 g. or $\frac{1}{4}$ the weight of the Pregl tube, and has an internal vol. <0·5 c.c. The modified tube has advantages over the Pregl tube in that it may be weighed much sooner after being polished, the weighing is more accurate, sweeping-out of O_2 and CO_2 is less likely to be incomplete, and transference to and from the balance-pan is much easier. The permanent rate of increase in wt. due to diffusion of moist air into the tube is only half that of the Pregl tube when the latter is charged with P_2O_5 on glass-wool. 12 tubes can be made and filled in 1 hr., the ends being kept sealed until the tube is required. A tube is used for three determinations and then discarded.   W. J. BOYD.

Volumetric determination of hydrogen peroxide in presence of potassium persulphate. V. M. NAYAK (J. Indian Chem. Soc., 1931, 8, 535—536).—Titrations of H_2O_2 with $KMnO_4$ are inaccurate if $K_2S_2O_8$ is present. The error may be corrected by determining in one sample the total available O by $FeSO_4$ and $KMnO_4$, and in another the $KMnO_4$ titre; residual $K_2S_2O_8$ in the second sample is then determined by $FeSO_4$ and $KMnO_4$. H. F. GILLBE.

Electrometric analysis of solutions of hypochlorites. M. ABRIBAT.—See B., 1931, 1047.

Determination of iodine in iodised common salt. A. GRONOVER and E. WOHNLICH.—See B., 1931, 1048.

Determination of fluorine in insecticides. C. M. SMITH, E. H. HAMILTON, and J. J. T. GRAHAM.—See B., 1931, 1048.

Determination of fluorine as calcium fluoride. E. CARRIÈRE and JANSSENS (Compt. rend., 1931, 193, 490—491; cf. this vol., 1023).—The amount of $CaCO_3$ formed by exposure to the air, or the presence of $(NH_4)_2CO_3$ in the aq. NH_3 used, in precipitating $CaCl_2$ with aq. NH_3 in the ordinary course does not exceed the experimental error, e.g., 2 mg. in dealing with 10 c.c. of $0·5M\text{-}CaCl_2$. To wash gelatinous CaF_2 thoroughly the ppt. must be boiled with H_2O 15 times.   C. A. SILBERRAD.

Effect of certain forms of silica on determination of fluorine by volatilisation method. D. S. REYNOLDS and K. D. JACOB (Ind. Eng. Chem. [Anal.], 1931, 3, 371—373).—SiO_2 gel, which has not been ignited above 1000°, and silicates which are decomposable by H_2SO_4 affect adversely the determination of F by the volatilisation method. A non-volatile compound, probably $SiOF_2$, is formed. SiO_2 gel which has been ignited at or above 1100° is as effective as quartz. The volatilisation method does not give trustworthy results for F in slags and certain natural phosphates containing acid-decomposable silicates.   E. S. HEDGES.

Volumetric determination of soluble sulphates. N. A. TANANAEV (J. Chem. Ind. Russ., 1931, 8, 939—949).—Excess of $N\text{-}Pb(NO_3)_2$ is added to the solution, the vol. is made up to 100 c.c., the solution is filtered after 5 min., and excess of Pb is determined in an aliquot part of the filtrate by titration with $0·5N\text{-}Na_2CO_3$ in the presence of phenolphthalein.
                    R. TRUSZKOWSKI.

Volumetric barium chromate method for [determination of] sulphates. T. R. ANDREWS (Ind. Eng. Chem. [Anal.], 1931, 3, 361—362).—The addition of $BaCrO_4$ to a sulphate solution, followed by titration of the liberated CrO_4'' with $FeSO_4$ and $KMnO_4$, is satisfactory for determining 2—200 mg. of SO_4''. Smaller quantities (0·5—2·0 mg.) may be determined by adding 2 mg. of Na_2SO_4 to the sample and deducting this from the amount recovered. H_2S and other reducing substances in the sample are oxidised by $KMnO_4$ before adding the $BaCrO_4$.
                    E. S. HEDGES.

Rapid determination of [ammonia and chlorine in] ammonium chlorostannate. J. HAEGE (Chem.-Ztg., 1931, 55, 791).—The solution is treated with 2% $Ba(OH)_2$ solution until neutral (phenol-phthalein), whereby $Sn(OH)_4$ is precipitated, the Ba in solution is then removed by addition of an excess of neutral, Cl'-free Na_2SO_4, and a portion of the filtrate is titrated with $AgNO_3$ (K_2CrO_4) for Cl'. A second portion is treated with 40% CH_2O solution and titrated with $0·1N\text{-}NaOH$ (phenolphthalein) to obtain the NH_4· content. Sn is determined by reduction to $SnCl_2$ and titration with I.
                    A. R. POWELL.

Precipitation of mercury in the Kjeldahl method. C. F. DAVIES and M. WISE (Cercal Chem., 1931, 8, 349—360).—In the precipitation of Hg in the Kjeldahl–Gunning procedure by means of alkali sulphides, a black ppt. indicates the use of sufficient precipitant. When $Na_2S_2O_3$ is employed, a brownish-black ppt. should be obtained, and excess of the reagent is not detrimental.   E. B. HUGHES.

Selenium as catalyst in determination of nitrogen by Kjeldahl method. M. F. LAURO (Ind. Eng. Chem. [Anal.], 1931, 3, 401—402).—Hg and $CuSO_4$ used as catalysts in the Kjeldahl process may with advantage be replaced by Se. E. S. HEDGES.

Determination of nitrate in water. W. MULDER.—See B., 1931, 1076.

Colorimetric determination of phosphorus. L. URBANEK (Mezög. Kutat., 1931, 4, 39—57; Chem. Zentr., 1931, i, 2643—2644).—The intensity of the blue colour obtained on reduction of phosphomolybdic acid is not exactly proportional to the P content of the solution, but a correction can be applied. The effect of [H·], acids, salts, and nature of reducing substance was studied.   A. E ELDRIDGE.

Determination of carbon dioxide in air. K. SARLÓ (Chem. Fabr., 1931, 397—398).—In the new apparatus described, a known vol. of air is drawn rapidly through aq. $Ca(OH)_2$ by an aspirator (2·2

litres in 12—13 min.). The solution is titrated with HCl and phenolphthalein. The apparatus is simple and may readily be constructed in portable form.

H. F. GILLBE.

Determination of carbon dioxide in the atmosphere. F. P. LEUSDEN (Z. Hyg., 1931, **112**, 606—612).—The sample is shaken in apparatus described with aq. $Ba(OH)_2$, which is subsequently titrated with HCl using thymolphthalein. The limit of error is 2%.

A. G. POLLARD.

Semi-microchemical determination of alkali metals in natural waters (bore waters) and silicates. K. L. MALAROV (Neft. Choz., 1930, 223—225).—The halides and org. substances are removed by evaporating 2—10 c.c. of the H_2O with 0·5—2 c.c. H_2SO_4; if SiO_2 is present the H_2O is first evaporated with HF. The residue, which is not heated above 350°, is treated with $Ba(OH)_2$; the alkaline earths are precipitated from the filtrate with $(NH_4)_2CO_3$ and aq. NH_3 in the cold, NH_4 salts are removed, and the residue is titrated with HCl (Me-orange). For silicates the material ($\equiv 0·03$—0·04 g. Na_2O) is decomposed in Pt with HF and H_2SO_4, and the residue treated as above. CHEMICAL ABSTRACTS.

Determination of traces of sodium in potassium salts. M. FŒRSTER.—See B., 1931, 1009.

Determination of silver in gold bars. F. MICHEL.—See B., 1931, 1056.

Gravimetric determination of calcium and magnesium using high temperatures, and the decomposition curves of carbonates and nitrates in an atmosphere of carbon dioxide. T. SOMIYA and S. HIRANO (J. Soc. Chem. Ind., Japan, 1931, **34**, 381—383B).—The following decomp. temp. in a current of CO_2 have been determined : (1) $CaCO_3$ (915—925°)$\longrightarrow$CaO ; $MgCO_3,(NH_4)_2CO_3,4H_2O$ (below 200°)$\longrightarrow MgCO_3$ (240—850°)$\longrightarrow$MgO ; Ca and Mg may therefore be determined simultaneously by weighing at 240°, 850°, and 925°. (2) $Ca(NO_3)_2$ (450—560°)$\longrightarrow$ $CaCO_3$ (915—925°)$\longrightarrow$CaO ; $Mg(NO_3)_2,H_2O$ (210—430°)$\longrightarrow$MgO ; Ca and Mg may be determined by weighing at 210°, 430°, 550°, and 925°. (3) $CaC_2O_4,4H_2O$ (50°)$\longrightarrow CaC_2O_4,H_2O$ (150°)$\longrightarrow$ CaC_2O_4 (440°)$\longrightarrow CaCO_3$ (920°)$\longrightarrow$CaO.

E. S. HEDGES.

Influence of potassium, ammonium, and hydrogen ions on Galeotti's reaction. B. KAMIEŃSKI and K. KARCZEWSKI (Rocz. Chem., 1931, **11**, 577—599).—Two breaks are observed on the potentiometric titration curve in the reaction between $ZnSO_4$ and $H_2Fe(CN)_6$ in presence of $K_2SO_4,(NH_4)_2SO_4$, or H_2SO_4 ; these are due, respectively, to the formation of $Zn_2Fe(CN)_6$ and $Zn_3X_2[Fe(CN)_6]_2$. As $[K^·]$, $[NH_4^·]$, or $[H^·]$ increases, the second break becomes more, and the first break less, distinct. $K^·$, $NH_4^·$, and $H^·$ may be present in variable amount in the ppt., as a result of which the reaction is not universally applicable to the determination of K ; in the determination of Zn in foundry practice by means of this method it is advantageous to ppt. Zn as $Zn_3(NH_4)_2[Fe(CN)_6]_2$, keeping the concentration of $NH_4^·$ below 0·4N.

R. TRUSZKOWSKI.

Quantitative optical spectral analysis of lead alloys. A. GUENTHER (Z. anorg. Chem., 1931, **200**, 409—418).—The systems examined were Li, Cu, Zn, Au, Tl, and Bi in Pb, and Ag in Sn. Tables are given showing pairs of lines in the emission spectra of the alloys suitable for the characterisation of alloys containing up to 10% of the other metal.

F. L. USHER.

Analysis of basic lead acetate solutions. N. SCHOORL (Chem. Weekblad, 1931, **28**, 586—589).—The refractive index and density may be employed to determine the composition of normal and basic Pb acetate solutions. The percentage of PbO in the solution is given by $K(d-1)/d$, where K is 101 for $3PbO,2Ac_2O$, 103 for $2PbO,2Ac_2O$, and 105 for $3PbO,Ac_2O$. If the composition of the solution is unknown it may be determined from the equations $(d-1)10^4 = 87x + 40y$ and $(n_D^{20} - 1·3330)10^5 = 80x + 160y$, where x and y are the percentages of PbO and Ac_2O, respectively, in the solution. The composition may be found also by the use of suitable indicators, since a solution of $3PbO,Ac_2O$ has p_H 7·4, one of $2PbO,Ac_2O$ p_H 7·8, and one of $3PbO,Ac_2O$ p_H 9 ; these vals. are almost independent of the concentration. H. F. GILLBE.

Rapid determination of small quantities of lead in calcium phosphate. J. R. NICHOLLS.—See B., 1931, 1009.

Volumetric and gravimetric determination of mercury as periodate. H. W. WILLARD and J. J. THOMPSON (Ind. Eng. Chem. [Anal.], 1931, **3**, 398—399).—Hg may be precipitated quantitatively as $Hg_5(IO_6)_2$ from 0·15N-HNO_3 or 0·1N-H_2SO_4. It may be weighed in this form or determined volumetrically with KI and $Na_2S_2O_3$. Moderate amounts of Al, Cd, Zn, Cu, Ni, Ca, and Mg do not interfere.

E. S. HEDGES.

Colorimetric determination of manganese. R. G. HARRY (Chem. and Ind., 1931, 796).—The blue coloration produced by adding $CH_2(C_6H_4·NMe_2)_2$ to a solution containing $Mn(OH)_2$ in AcOH provides a satisfactory method for determining Mn. The colour standard is reasonably stable, but slowly fades. It may be replaced by a set of colour standards, which keep for a long time and match the colours produced (ranging from pale blue to purple), prepared by mixing solutions of crystal-violet and methylene-blue.

E. S. HEDGES.

Volumetric determination of manganese after oxidation by periodate. H. W. WILLARD and J. J. THOMPSON (Ind. Eng. Chem. [Anal.], 1931, **3**, 399—401).—Mn is oxidised to $NaMnO_4$ by means of $NaIO_4$ in H_3PO_4 or H_2SO_4 solution, the excess of $NaIO_4$ is removed by precipitation as $Hg_5(IO_6)_2$, and the $NaMnO_4$ is determined by titration with standard $FeSO_4$. Co, Ce, and Cl′ must be absent and the amount of Cr must be <1 mg. Directions are given for the application of the method to the determination of Mn in Fe or steel, Fe ore, and bronze.

E. S. HEDGES.

Determination of manganese in cobalt steels. F. SPINDECK.—See B., 1931, 1054.

Reversible oxidation indicator of high potential especially adapted to oxidimetric titrations. G. H. WALDEN, jun., L. P. HAMMETT, and R. P. CHAPMAN (J. Amer. Chem. Soc., 1931, **53**, 3908 ; cf.

A., 1899, i, 387).—The intensely red Fe¨ o-phenanthroline complex ion is oxidised reversibly by $Ce(SO_4)_2$, or $K_2Cr_2O_7$ in H_2SO_4 or HCl, to the less intensely blue Fe¨ complex ion. The mol. potential of the indicator system is 1·14 volts. The indicator is stable in acid solution and a quantity equiv. to 0·01 c.c. of 0·1N solution is satisfactory in the titration of Ce¨¨¨ or Cr_2O_7'' with Fe¨. Common metallic ions, including Hg¨, do not interfere. The Fe¨ dipyridyl complex is a less satisfactory indicator owing to rapid reaction with acids.

J. G. A. GRIFFITHS.

Electrolytic determination of cobalt. D. H. BROPHY (Ind. Eng. Chem. [Anal.], 1931, 3, 363—365). —The solution recommended contains 50 c.c. of aq. NH_3, 5 g. of NH_4Cl, and 0·3—0·4 g. of $NaHSO_3$ in 80—100 c.c. With a rotating anode (800—1000 r.p.m.) and a gauze cathode, using a current density of 4—7 amp. per sq. dm., it is possible in 30 min. to deposit 15—160 mg. of Co in a bright, adherent form. The amount of S in the deposit is negligible. The use of org. acids, N_2H_4,H_2SO_4(or HCl), or NH_2OH,HCl in place of $NaHSO_3$ is unsatisfactory.

E. S. HEDGES.

Ultra-violet absorption of mixtures of chromate and dichromate solutions. N. R. TAWDE (J. Indian Chem. Soc., 1931, 8, 499—501).—Ultraviolet spectrophotometric determinations (A., 1930, 992) of CrO_4'' and Cr_2O_7'' in dil. solution agree fairly satisfactorily with the analytical vals.

H. F. GILLBE.

Determination of titanium as phosphate. J. C. GHOSH (J. Indian Chem. Soc., 1931, 8, 695—698).—0·5—1·0 g. of the dried and powdered Ti ore is fused with Na_2CO_3 or treated with HF and H_2SO_4 and the resulting Na_2TiO_3 is treated with boiling H_2O, filtered, and washed, and an insol. acid titanate, $2Na_2O,9TiO_2,5H_2O$, formed. This is dissolved in 30 c.c of boiling dil. H_2SO_4 (1 : 5) and the solution diluted to 200 c.c., cooled, nearly neutralised with aq. NH_3, and treated with 20 c.c. of 20% aq. $(NH_4)_2HPO_4$. Any ppt. formed on further dilution to about 400 c.c. is redissolved in a slight excess of H_2SO_4, 10 g. of $Na_2S_2O_3$ and 10 c.c. of AcOH are added to reduce the Fe, and the solution is boiled for about ½ hr. The ppt. of TiO_2,HPO_3 is filtered, washed with H_2O, ignited, and weighed as a pyrophosphate, $2TiO_2,P_2O_5$. HCl may be used in place of H_2SO_4, but long boiling with HCl may ppt. metatitanic acid. The results compare favourably with those obtained by the oxide method, and the phosphate method should be used when P_2O_5 is already present.

M. S. BURR.

Determination of vanadium in high-speed steel. E. FÄRBER.—See B., 1931, 1054.

Reaction of vanadates. Determination of tungsten with tetramethyldiaminodiphenylmethane. M. PAPAFIL and R. CERNATESCO (Ann. Soc. Univ. Jassy, 1931, 16, 526—528).—Addition of a solution of $CH_2(C_6H_4\cdot NMe_2)_2$ in AcOH, of p_H 3·5, to a neutral solution containing vanadate yields an immediate yellow ppt. which gradually turns green; the *compound* formed is $(VO_3)_4C_{17}H_{22}N_2$. The limiting concentration of vanadate is about 0·05 g. per litre.

For determination of W with this reagent any excess of NH_4 salts should be removed; the ppt. is dried at 110° and ignited to oxide.

H. F. GILLBE.

Determination of a small amount of antimony in presence of a large amount of copper. S. MAKISHIMA (J. Soc. Chem. Ind., Japan, 1931, 34, 322—323B).—A quantity of solution containing a few mg. of Sb is neutralised, 5 c.c. of 5% $MnSO_4$ solution are added, the mixture is boiled, and N-$KMnO_4$ solution added. The ppt. of MnO_2 collects the Sb by adsorption. It is washed, dissolved in dil. H_2SO_4 containing a little H_2O_2, Na_2SO_3 is added, and the SO_2 boiled off. The solution is brought to 0·02—0·1N acidity, and the coloration developed on addition of Folin's reagent $(Na_2MoO_4 + Na_2HPO_4)$ is compared with that given by a known Sb solution.

C. IRWIN.

Indirect determination of bismuth. C. V. BORDEIANU (Ann. Sci. Univ. Jassy, 1931, 16, 546—550).—Chlorides are removed by precipitation with $AgNO_3$, the Bi is precipitated by $(NH_4)_2HPO_4$, and the excess of phosphate is determined colorimetrically.

H. F. GILLBE.

Adiabatic calorimetry. S. W. PARR and W. D. STALEY (Ind. Eng. Chem. [Anal], 1931, 3, 396—397).— Tests of the efficiency of a vac. jacket for heat-insulation are recorded.

E. S. HEDGES.

Application of electric thermometers with crossed resistances to ebullioscopic and tonometric measurements. T. BYLEWSKI (Rocz. Chem., 1931, 11, 552—568).—A modification of Jaeger and Steinwehr's resistance thermometer, giving an accuracy of 0·001° over the range 0—250°, is described. A resistance box and commutator for use with the above thermometer are also described.

R. TRUSZKOWSKI.

Photo-electric cell thermoregulator. F. G. BRICKWEDDE and R. B. SCOTT (Physical Rev., 1930, [ii], 35, 670).—A photo-electric regulator which automatically maintains temp. const. to 0·001° between 0° and the temp. of liquid air has been constructed.

L. S. THEOBALD.

Low-temperature thermostat. H. W. FOOTE and G. AKERLOF (Ind. Eng. Chem. [Anal.], 1931, 3, 389—390).—By means of a small electrical refrigerating unit and a Hg-PhMe regulator the temp. of the bath can be maintained within ±0·015° at any desired val. between 0° and min. room temp.

E. S. HEDGES.

Thermostats. V. Measurements of stirrer performance. S. KAMBARA, S. OYAMADA, and M. MATSUI (J. Soc. Chem. Ind., Japan, 1931, 34, 361—367B).—A photo-electric colorimetric procedure for measuring stirring efficiency is described. An examination of 13 types of stirrers has shown that the propeller type, used with a proper vessel, is the most effective.

E. S. HEDGES.

Balanced thermo-couple and filter method of ultra-violet radiometry, with practical applications. W. W. COBLENTZ, R. STAIR, and J. M. HOGUE (Bur. Stand. J. Res., 1931, 7, 723—749).— One receiver of a thermocouple is covered with a filter excluding ultra-violet light, and the other with

a window transparent to ultra-violet light, which exactly balances the transmission losses of the exclusion filter throughout the remaining part of the spectrum. On exposing both receivers simultaneously to radiation the deflexion of the galvanometer gives a measure of the ultra-violet light intensity. Applications of the method are discussed.

E. S. HEDGES.

Multiple spark stand for quantitative spectrum analysis. L. J. SPENCER (J. Sci. Instr., 1931, 8, 229—232).—The intensities of the lines produced by the " unknown " sample are compared with those of a series of standard samples. The latter are mounted on a disc which can be rotated so that each sample in turn is connected in series with the one under test. C. W. GIBBY.

Direct-reading two-crystal spectrometer for X-rays. F. K. RICHTMYER, S. W. BARNES, and E. RAMBERG (Physical Rev., 1930, [ii], 35, 1428).—Abs. measurements of wave-lengths can be obtained with high precision. L. S. THEOBALD.

Instrument for high-voltage X-ray spectrography and radiography. F. SILLERS, jun. (Physical Rev., 1930, [ii], 35, 1428).—X-Ray spectrograms of coarse-grained, polycryst. material, e.g., high-Si sheet steel 0·02 in. thick, can be obtained in less than 1 hr. by direct transmission using a voltage of 200 kv. L. S. THEOBALD.

Self-recording spectrometer. H. M. RANDALL and J. STRONG (Rev. Sci. Instr., 1931, [ii], 2, 585—599).—An instrument for emission and absorption spectra over the entire prism or grating spectral region, and capable of enclosure in an evacuated chamber, is described. Absorption band curves are given for NH_3 and MeI at various pressures.

N. M. BLIGH.

Twenty-one foot vacuum spectrograph for the extreme ultra-violet. G. R. HARRISON (Rev. Sci. Instr., 1931, [ii], 2, 600—610).—The spectrograph body and camera box can be evacuated separately. 1 hr. exposures give spectrograms of 2·7 Å. dispersion per mm., the 2000—1000 Å. range being recorded on a 16-in. plate. High resolving power has been obtained in hot spark spectra of the elements of the first long period. The design is primarily for intensity measurements in the Schumann region.

N. M. BLIGH.

X-Ray powder diffraction apparatus. T. M. HAHN (Rev. Sci. Instr., 1931, [ii], 2, 626—631).—The time required to produce a readable diffraction pattern is minimised by utilising a larger vol. of the sample, and the formation of weaker spots nearer the sample. N. M. BLIGH.

Simple improved method for reducing Fabry-Perot observations. S. TOLANSKY (J. Sci. Instr., 1931, 8, 223—225).—An accuracy of 0·001 of a wave no. can be obtained using 4- or 5-figure log. tables.

C. W. GIBBY.

Photomicrographs with [light of] wave-length 312 mμ. A. P. H. TRIVELLI and E. LINCKE (Z. wiss. Phot., 1931, 30, 85—87).—Photomicrographs are given of sections of calf skin and of a leaf of *Nerium oleander*, taken at 312 and 546 mμ.

J. LEWKOWITSCH.

Ultra-violet microscopy. B. K. JOHNSON (J. Roy. Micros. Soc., 1931, [iii], 51, 268—271).—Photographs illustrating the improved results obtainable with ultra-violet light are reproduced.

C. W. GIBBY.

Photographic method of examining crystals. A. SCHUBNIKOV (Z. Krist., 1931, 78, 111—135).

Photo-electric determination of the turbidity of liquids. P. JAKUSCHOFF (Z. Ver. Deut. Ing., 1931, 75, 426—428; Chem. Zentr., 1931, i, 3147).—A K cell, with Ag anodes, in H_2 (4 mm.) is employed. The turbidity, concentration, or colour of liquids is easily and rapidly determined. A. A. ELDRIDGE.

Mixed-colour colorimeter. A. THIEL (Sitzungsber. Ges. Nat. Marburg, 1930, 65, 159—167; Chem. Zentr., 1931, i, 3147).—The advantages of the method, which depends on the achievement of equality of tint and not of intensity of colour, are discussed. It is specially suitable for p_H determinations.

A. A. ELDRIDGE.

Measurement of the brightness of radioactive luminous compounds. H. F. MEACOCK and G. E. V. LAMBERT (J. Sci. Instr., 1931, 8, 214—220).—Two instruments are described, for use respectively with surfaces of diameter larger or smaller than 6 mm. The reproducibility is 2% with the former and 10% with the latter. C. W. GIBBY.

Applications of thermionic valves in the technique of physico-chemical measurements. W. HILTNER (Chem. Fabr., 1931, 389—392, 398—400).—The theory of the thermionic valve is given, together with details, including circuit diagrams, of the operation of such valves for the production of oscillatory currents for dielectric const. determinations with electrolytic conductors and of a.c. for measurement of the conductivity of electrolytes, as relays for the control of thermostats and for the measurement of small pressures, as rectifiers and amplifiers of a.c., as amplifiers for, e.g., ionisation currents, as potentiometers for p_H measurements and potentiometric titrations, and as null instruments for e.m.f. measurements by a compensation method.

H. F. GILLBE.

Capillary glass electrode. W. J. YOUDEN and I. D. DOBROSCKY (Contr. Boyce Thompson Inst., 1931, 3, 347—362).—The construction and use of thin-walled glass electrodes are described.

A. G. POLLARD.

Development of Kohlrausch's conductivity apparatus with the aid of electron-tubes. E. GÖTTE and W. SCHRAMEK (Z. Elektrochem., 1931, 37, 820—823).—An improved apparatus is described.

E. S. HEDGES.

Galvanometer for measurement of conductivity of solutions. G. GOLLNOW (Chem.-Ztg., 1931, 55, 827—828).—The instrument resembles the D'Arsonval galvanometer, but the moving coil has no core and the field magnet is of laminated Fe provided with a field coil which is energised (at 110 volts) from a transformer connected to the mains. The e.m.f. for the bridge circuit is obtained by shunt connexion across an adjustable resistance placed in series with the field coil. The moving coil of the

galvanometer is connected in place of telephones in the bridge circuit. Zero corrections may be made for errors of the pointer and for errors due to the magnet. The instrument may also be used for d.c.
H. E. BLAYDEN.

Sensitive direct-reading mercury manometer. H. W. MELVILLE (J.C.S., 1931, 2509—2511).—The vertical displacement of an inverted glass cup floating on Hg is used to measure pressure differences down to 0·001 mm. Hg.
H. J. EMELÉUS.

Simple pressure regulator. J. D. A. JOHNSON (J.C.S., 1931, 2523—2524).—A diagram is given of a simple apparatus for controlling the pressure to a few mm. of Hg in distillations at reduced pressures.
H. J. EMELÉUS.

Gas-pressure regulator. A. C. ROBERTSON (Ind. Eng. Chem. [Anal.], 1931, 3, 383—384).—The apparatus permits const. pressure regulation for small loads and, by the use of two such regulators, gases may be mixed in any proportion.
E. S. HEDGES.

Simple apparatus for analytical control. R. FEIBELMANN (Chem. Fabr., 1931, 405—407, 414—416). —By the use of suitably calibrated measuring cylinders the approx. active contents of solutions of, e.g., NaOCl, H_2O_2, $NaBO_3$, and $Na_2S_2O_4$ may be determined titrimetrically. A simple apparatus is described in which the reduction val. of a vat dye is determined by measuring the vol. of air necessary for complete oxidation of 10 c.c. of the solution. The fatty acid content of such materials as soaps and Turkey-red oil may be determined by hydrolysis in a 200-c.c. flask having a long graduated neck; when hydrolysis is complete warm H_2O is added and the length of the oily layer in the neck is measured.
H. F. GILLBE.

High-vacuum pressure control apparatus. T. L. HO (Proc. Nat. Acad. Sci., 1931, 17, 548—550).— The pressure is indicated by an ionisation gauge, which operates a galvanometer. A contact attached to the latter controls a thermionic amplifier, which in turn operates a relay, opening a leak.
C. W. GIBBY.

Elementary apparatus for static determination of the partial pressures of gases in solution. U. M. NAYAK and S. LAKHMINARAYANAN (J. Indian Chem. Soc., 1931, 8, 531).—A burette and a side tube are fitted to a large empty bottle. A known vol. of, e.g., SO_2 solution is placed in the bottle, the whole is shaken, and a known vol. of the solution is then withdrawn and titrated. From the fall of concentration and the vol. of the apparatus the partial pressure may be calc.
H. F. GILLBE.

Apparatus for absorption of hydrogen by silver permanganate according to the method of Hein and Daniel. B. RASSOW and L. WOLF (Chem. Fabr., 1931, 407).—The advantage of a mechanical shaking device is noted. The evolution of O_2 observed during the absorption of H_2 is ascribed to insufficient washing of the Ag catalyst; the quantity of O_2 evolved may be reduced by shaking the freshly filled pipette with air or N_2 before introducing the mixture to be analysed. The method is recommended for illuminating gas, cracked gas, and N_2-H_2 mixtures.
H. F. GILLBE.

Gas absorption pipette. A. C. EGERTON and L. M. PIDGEON (J. Sci. Instr., 1931, 8, 234).—The pipette consists of two bulbs joined by a narrow neck. The reagent is drawn down into the lower one by lowering a Hg reservoir, and can be forced up again in the form of a fountain. Samples and reagents can be admitted through a side-tube which can be sealed with Hg. Honey has been found satisfactory as a greaseless lubricant.
C. W. GIBBY.

Water distillation apparatus. A. SCHLEEDE and E. KÖRNER (Chem.-Ztg., 1931, 55, 808).—The apparatus previously described (A., 1930, 884) is modified by replacing the Cu distillation flask with a flask of " R " glass having an inlet at the bottom through which the overflow cooling H_2O from the condenser enters the flask which is heated with a ring burner.
A. R. POWELL.

Reflux condensers for extraction and distillation apparatus. C. ZINZADZE (Bull. Soc. chim., 1931, [iv], 49, 1204—1205).—(1) The condensed vapours flow over the tube from which the vapour issues to the condenser and are returned to the material under extraction through a three-way cock which allows the solvent to be eliminated when the extraction is complete. (2) The condensate falls into a receiver, round which the vapours ascend to the condenser, and is similarly returned to the material under extraction through a three-way cock.
R. BRIGHTMAN.

Methods of using the Liebig condenser. Asbestos shields for distilling flasks. I. ENDLER (Chem. Ztg., 1931, 55, 799).—Common errors in the use of glass condensers are noted and the correct method is described. A disc of asbestos, with a central circular depression conforming to the shape of the bottom of the flask, is recommended as a shield for distilling flasks; it may readily be formed from wet 2—3-mm. asbestos sheet. The flat portion should be wide enough to prevent direct heat from the burner reaching the flask.
H. F. GILLBE.

Differential ebullioscope fitted with a rectifying column, and its application. W. SWIENTOSŁAWSKI (Rocz. Chem., 1931, 11, 545—551).—The above apparatus serves for the determination of the difference between the temp. of ebullition of a liquid and of condensation of its vapours after passage through the column. The technique of making comparative measurements, whereby the b. p. of a liquid before and after purification is compared with that of H_2O at the same pressure, is described.
R. TRUSZKOWSKI.

Still-head for laboratory columns. E. B. KESTER and R. ANDREWS (Ind. Eng. Chem. [Anal.], 1931, 3, 373).
E. S. HEDGES.

Gauze-plate laboratory rectifying column. S. PALKIN (Ind. Eng. Chem. [Anal.], 1931, 3, 377—378).—The construction of a column containing plates of Ni wire-gauze is described. Data are given in illustration of its efficiency.
E. S. HEDGES.

Economy of time in laboratory distillation. D. F. STEDMAN (Canad. J. Res., 1931, 5, 455—465).— A mathematical consideration of fractional distillation is approx. verified with MeOH-EtOH mixtures.
R. S. CAHN.

Pump for water vapour at low pressure. P. SCHLUMBOHM (Chem. Fabr., 1931, 429—430).—A detailed account of a combined pump and continuously operating H_2SO_4 absorber for H_2O vapour, which is especially suitable for the evaporation at low temp. of biochemical and other temp.-sensitive solutions; it may be employed also as a refrigerating machine.
H. F. GILLBE.

Transparent cellulose covers for Nessler comparison tubes. E. ZIMBON (Ind. Eng. Chem. [Anal.], 1931, 3, 356).—Cellophane covers are recommended for the tubes containing the colour standards, thus obviating errors due to the removal of stoppers.
E. S. HEDGES.

Solid carbon dioxide in laboratory technique. D. H. KILLEFFER (Ind. Eng. Chem. [Anal.], 1931, 3, 386—387).—Applications of solid CO_2 to laboratory practice are suggested. E. S. HEDGES.

Large-capacity Soxhlet extractor. V. H. MORRIS (Chemist-Analyst, 1931, 20, No. 4, 18—19).—The outer container (32×17 cm.) is of Cu, Sn, or Al; the inner vessel is $13 \cdot 5 \times 11$ cm. A 3-litre flask filled with H_2O and placed on top serves as a condenser.
CHEMICAL ABSTRACTS.

Microgravimetric analyses. P. L. KIRK and R. CRAIG (Ind. Eng. Chem. [Anal.], 1931, 3, 345—347).—An apparatus which permits precipitation and filtration to be carried out in the same vessel is described. No loss of ppt. occurs in the determination of SO_4'', halide, or PO_4''' in very small samples. E. S. HEDGES.

Alloys for vacuum-tight glass–metal joints. D. E. OLSHEVSKY (Physical Rev., 1930, [ii], 35, 1424). —Alloys containing 50% Pb, 37·5% Bi, 12·5% Sn, and 31·1% Pb, 12·5% Sn, 47% Bi, 9·4% Cd have little or no tendency to crack glass, and when backed by cement form strong, rigid, and replaceable vac.-tight joints. L. S. THEOBALD.

Electromagnet for investigation of the magnetic properties of atoms and molecules. E. J. SHAW (Rev. Sci. Instr., 1931, [ii], 2, 611—617).—A design to prevent overheating, to allow an increased region of field, to minimise stray field, and to allow easy assembly is described. N. M. BLIGH.

Representation of the results of investigations of mixtures. G. BRUHNS (Chem.-Ztg., 1931, 55, 798—799).—Partly an account of a method described previously, and applicable to, e.g., natural waters, with details of its use in the case of potash mother-liquors.
H. F. GILLBE.

Geochemistry.

Analysis of the springs at Răducăneni [Rumania]. R. CERNATESCO and A. MAYER (Ann. Sci. Univ. Jassy, 1931, 16, 529—532).—Detailed analyses are given. H. F. GILLBE.

Thermal waters of the north-east spring at Termini Imerese. G. MASSARA and S. CAPUANO (Annali Chim. Appl., 1931, 21, 403—418).—The composition of this spring is substantially that found by Oliveri (1894), except that Li, Rb, and Cs are now detectable. Physical and physico-chemical data are also given. T. H. POPE.

Buffer capacity of sea-water. T. G. THOMPSON and R. U. BONNAR (Ind. Eng. Chem. [Anal.], 1931, 3, 393—395).—The buffer capacity of sea-water is defined as the no. of millimol. of $H^.$ which a unit vol. of sea-water will neutralise when an excess of standard acid is added. Normal sea-waters have a fairly const. buffer capacity, but the val. varies with land drainage, effects of biological phenomena, and industrial pollution. Buffer capacity may be only partly dependent on the concentration of CO_3'' and HCO_3', and the total CO_2 cannot be determined by direct acidimetry. E. S. HEDGES.

Bacteriological precipitation of lime in tropical sea. H. FISCHER (Ber. deut. Bot. Ges., 1931, 49, 357—359).—Sedimentation of $CaCO_3$ and $MgCO_3$ in sea-water may result from decay of various organisms, from the action of CO_2 and NH_3, produced by decay, on Ca salts, and from bacteriological denitrification and desulphurisation. The cyclic processes which take place are outlined. H. F. GILLBE.

Tidal flat and salt marsh studies in Nelson Haven. II. Soil chemistry of the Nelson mud flat. B. W. DOAK (N.Z. J. Sci. Tech., 1931, 13, 1—11).—Analyses of sol. matter, exchangeable bases, and p_H vals. at varying soil depths are recorded. The flora of these soils is controlled mainly by their salinity; the Mg content is closely related. The salts are characterised by a low exchangeable Ca and high exchangeable Mg content. A. G. POLLARD.

Analysis of the powder deposited at Jassy in February 1929. M. PONI and R. CERNATESCO (Ann. Sci. Univ. Jassy, 1931, 16, 533—535).—Approx. 5 g. of dust per sq. m. were deposited in 2 days during a dust storm; the material consisted largely of SiO_2 (72·6%), Al_2O_3 (7·76%), Fe_2O_3 (4·95%), alkalis and alkaline earths, and P_2O_5 (1·71%).
H. F. GILLBE.

Mean composition of meteorites. I. I. ZASLAVSKI (J. Gen. Chem. Russ., 1931, 1, 406—410).—The mean ratio in meteorites of silicate : metal : troilite$=1 : 0·25 : 0·07$; this result is in good agreement with Fersman's, but not with Farrington's, figures. R. TRUSZKOWSKI.

Tilden meteorites. A. R. CROOK and O. C. FARRINGTON (Trans. Ill. Acad. Sci., 1930, 22, 442—449).—The meteorite (July 13, 1927) contained Fe 6·38, N 0·31, Co 0·02, S 2·31, P 0·15, SiO_2 41·22, Al_2O_3 3·69, FeO 22·28, NiO 0·99, CoO 0·04, MgO 22·30, CaO 0·91, Na_2O 0·53, K_2O 0, H_2O 0·03, less O for S and P 1·38; total 99·78%. CHEMICAL ABSTRACTS.

Mean composition of the earth. I. I. ZASLAVSKI (J. Gen. Chem. Russ., 1931, 1, 401—405).—The % composition of the earth, computed on the basis of the mean composition of meteorites, agrees well with

Washington's figures, arrived at by a different method. R. TRUSZKOWSKI.

Crystal type of barytes in relation to minerogenetic succession. G. KALB and L. KOCH (Z. Krist., 1931, **78**, 169—170).

Dehydration of natural ferric hydroxides. S. GOLDSZTAUB (Compt. rend., 1931, **193**, 533—535).—Goethite and lepidocrocite have respectively a 4·64, 3·87; b 10·0, 12·4; c 3·03, 3·06 Å.; space-groups $V_h^{16}bnm$, V_h^1mmm (cf. A., 1929, 988). On dehydration goethite passes into a mass of small crystals of hæmatite oriented in parallel. When slowly heated to 460° fibrous lepidocrocite of Chizeul acquires the structure of magnetite, and the coeff. of magnetisation increases 100 times; when heated rapidly to 440° it acquires that of hæmatite, and the coeff. increases only 50-fold. A crystal from Siegen when heated rapidly did not disintegrate, and became magnetic (cf. A., 1925, ii, 845; 1928, 503).
C. A. SILBERRAD.

Vanadiferous nodules in the Permian beds of South Devon. G. E. L. CARTER (Min. Mag., 1931, **22**, 609—613).—Greenish-black nodules surrounded by a bleached pale green aureole occur in certain beds of red clay near Budleigh Salterton and Exmouth. Analyses show the material to be a siliceous clay with V_2O_5 13·96% in the dark portion and 1·91% in the pale green aureole. The adjacent red clay contains 0·17% V_2O_5. L. J. SPENCER.

Chemical, optical, and X-ray study of nepheline and kaliophilite. F. A. BANNISTER [with M. H. HEY] (Min. Mag., 1931, **22**, 569—608).—Detailed determinations of the optical, density, and X-ray data were made for a number of selected specimens of nepheline from Vesuvius and of elæolite and "pseudonepheline," and chemical analyses were made on the same samples of material. A strict correlation of the various properties was thus possible. The hexagonal unit cell of dimensions a 9·94—9·99, c 8·31—8·38 Å. contains a const. no. (32) of O atoms, whilst the no. of other atoms varies, the contents of the unit cell being $Si_{16-n}Al_n(Na,K,\frac{1}{2}Ca)_nO_{32}$, where n ranges from 6·6 to 8·2. The cell dimensions increase slightly with the content of K, the higher vals. quoted above being for "pseudonepheline," which is richest in K. In kaliophilite the unit cell is much larger, a 26·7—27·0, c 8·49—8·51 Å., and contains 54 $KAlSiO_4$. A kaliophilite structure built up from nepheline cells is suggested. L. J. SPENCER.

Brown hornblende and biotite from Shabō-zan, Taiwan. T. ICHIMURA (Min. Mag., 1931, **22**, 561—568).—Chemical analyses and optical data are given for brown hornblende and basaltic hornblende, the former occurring in brown andesite and the latter in grey andesite, of the Shabō-zan volcano in Taiwan (Formosa). The brown hornblende and biotite have arisen by the heating and oxidation of the basaltic varieties. L. J. SPENCER.

Residual liquids of crystallising magmas. C. N. FENNER (Min. Mag., 1931, **22**, 539—560).—A general discussion of the process of crystallisation-differentiation in basaltic magmas, with criticism of the views of other authors. L. J. SPENCER.

Wearing of rocks in water. F. W. FREISE (Tsch. Min. Petr. Mitt., 1931, **42**, 48—58).—Experiments on the wearing hardness of various Brazilian rocks in H_2O are continued on the same lines as previously used for minerals (A., 1931, 459).
L. J. SPENCER.

Iron ores of the Sulin district in the Donetz coal-basin. D. SERDJUTSCHENKO (Tsch. Min. Petr. Mitt., 1931, **42**, 27—47).—Analyses are given of the limonitic ores, which were formed by metasomatic replacement of limestone. L. J. SPENCER.

Determination of acid plagioclases by the zonal method. H. EBERT (Tsch. Min. Petr. Mitt., 1931, **42**, 8—26).—Measurement on the universal microscope-stage of the extinction angles in the zone perpendicular to the face (010) affords a means of determining the twin law and the percentage of the anorthite mol. in the plagioclase felspars.
L. J. SPENCER.

Proposed change in calculation of norms of rocks. T. F. W. BARTH (Tsch. Min. Petr. Mitt., 1931, **42**, 1—7).—In the system of Cross, Iddings, Pirsson, and Washington (1902) chemical analyses of rocks are calc. in amounts of arbitrarily selected "normative" minerals (not necessarily actually present in the rock). Better results are obtained for the "norm" if the "normative" pyroxenes are expressed as $CaSiO_3$, $MgSiO_3$, and $FeSiO_3$, and the olivine mols. in terms of Mg_2SiO_4 and Fe_2SiO_4.
L. J. SPENCER.

Forms and places of occurrence of pyrites. L. TOKODY (Z. Krist., 1931, **80**, 255—348).—A list of 238 definite and 221 uncertain or vicinal forms of pyrites with place of origin; of 272 places of occurrence with the forms found at each, with discussion thereon, and a bibliography of 706 references.
C. A. SILBERRAD.

Rosickyite : natural nacreous sulphur. J. SEKANINA (Z. Krist., 1931, **80**, 174—189).—On the clay-covered inner walls of concretions, consisting of a limonite crust interspersed with radiating aggregates of pyrite, occurring in clay deposits in chalk at Kunstadt and Lettowitz (Czechoslovakia), are found small (>0·5 mm.), slightly yellow crystals of adamantine lustre, easily sol. in C_6H_6, CH_2I_2, and CS_2. They are monoclinic, $a:b:c=1·0606:1:0·7094$, β 91° 48', agreeing with Muthmann's results (cf. Z. Krist., 1890, **17**, 336; A., 1927, 216) for nacreous S, or S III. The crystals readily pass into the rhombic modification, but as found are free therefrom, and are clearly the result of slow decomp. of pyrites. Results are confirmed by comparison with artificial nacreous S, and Muthmann's different result for the extinction angle is shown to be due to change to rhombic S, the course of which is traced. The name rosickyite is proposed. It is probably identical with the variety of S found in the crater of Stromboli by Panichi in 1911 (cf. Zambonini, Z. Krist., **54**, 393). C. A. SILBERRAD.

Optical study of tarbuttite. H. BUTTGENBACH and J. MELON (Bull. Acad. roy. Belg., 1931, [v], **17**, 892—901).—The orientation of the principal axes and the coeff. of refraction and birefringence of tarbuttite have been measured. J. W. SMITH.

Kolm. R. C. Wells and R. E. Stevens (J. Wash. Acad. Sci., 1931, **21**, 409—414).—The Pb : U ratio is 0·061, whence the age is calc. to be $4·58 \times 10^8$ years. The kolm (from Sweden) is only slightly permeable to gases. C. W. Gibby.

Diopside and tremolite of Monte Spinoza, Campiglia. F. Rodolico (Atti R. Accad. Lincei, 1931, [vi], **13**, 705—710).—The analysis of a sample of tremolite conformed to the formula $CaMg_3(SiO_3)_4$, but to the formula $H_2Ca_2Mg_5(SiO_3)_8$ if the possibility of the substitution of SiO_2 by Al_2O_3 is admitted. If the substitutions postulated by Warren (A., 1930, 844) are recognised, the second formula appears to be correct. The analysis and crystallographic data of a specimen of diopside are described.
H. F. Gillbe.

Dolomite problem. H. Udluft (Z. Deut. Geol. Ges., 1931, **83**, 1—13; Chem. Zentr., 1931, i, 2599—2600).—The solubility curves of $CaCO_3$ and $MgCO_3$ in relation to the CO_2 partial pressure of the solvent intersect at a point below which $CaCO_3$ is less sol. than $MgCO_3$. In sea-water vals. usually below this point are obtained; when the val. corresponds with the point of intersection dolomite separates. Dolo-

mitisation of $CaCO_3$ therefore takes place when the CO_2 partial pressure rises above the intersection point.
A. A. Eldridge.

Classification of magmatic rocks. E. Tröger (Neues Jahrb. Min., 1931, A, **62**, 249—330; Chem. Zentr., 1931, i, 2599).—The classification depends on a projection system relating to the composition.
A. A. Eldridge.

Strontium content of magmatic rocks. W. Noll (Naturwiss., 1931, **19**, 773—774).—The Sr contents of magmatic minerals and rocks containing Ca have been determined. Ca and Sr are isolated chemically and the relative wts. of CaO and SrO are determined by means of X-ray spectroscopy. The SrO content of pyroxene is 0·10%, of labradorite 0·12%, of larvikite felspar 0·36%, and of sanidine 0·48%. W. R. Angus.

Evidence of the presence of element 87 in pollucite and lepidolite ores. F. Allison and E. J. Murphy (Physical Rev., 1930, [ii], **35**, 285).—Application of the magneto-optic method of analysis (A., 1930, 1541) to these ores shows min. corresponding with eka-Cs; several isotopes are indicated.
L. S. Theobald.

Organic Chemistry.

Determination of small quantities of methane. H. R. Ambler (Analyst, 1931, **56**, 635—637).—H_2 and CO are oxidised by powdered CuO in an electric furnace at about 300° and the H_2O and CO_2 formed are removed by absorption with $CaCl_2$ and ascarite, or measured, as desired. The CH_4 is determined by burning with O_2 in presence of Pt wire at a bright yellow heat. The apparatus is described.
T. McLachlan.

Catalytic oxidation of paraffins. M. Goswami and S. K. Chatterjee (J. Indian Chem. Soc., 1931, **7**, 533).—Passage of the vapour of paraffin (m. p. 49°) in a current of air over reduced Ni gives mixed aldehydes, probably of the C_8 to C_{11} series.
R. S. Cahn.

F. p. of organic compounds. XIII. L. Deffet.—See this vol., 1361.

Reactions of addition to unsaturated organic compounds. P. Pratesi (Atti R. Accad. Lincei, 1931, [vi], **13**, 779—784).—The regularities in the mode of formation of additive compounds by org. compounds of different types pointed out by Markovnikov and by Ipatiev are explained on the basis of the electronic theory of valency. T. H. Pope.

Orientation in the addition of halogens and hydrogen halides to simple ethylene derivatives. I. Additions with iodine monochloride. C. K. Ingold and H. G. Smith. **II. Addition of hydrogen halides to propylene and Δ^a-pentene.** C. K. Ingold and (Miss) E. Ramsden (J.C.S., 1931, 2742—2746, 2746—2752).—I.Propylene reacts with ICl in dil. HCl, giving a mixture (A) of 69% of β-chloro-α-iodopropane (I) and 31% of α-chloro-β-iodopropane (II); the amounts of (I) and (II) are determined by treatment of A with EtOH–KOH at 0° and subsequent

refractometric analysis of the resultant mixture of α- and β-chloro-Δ^a-propenes. Styrene and ICl in presence of conc. HCl and CH_2Cl_2 afford a product containing at least 95% of α-chloro-β-iodo-α-phenylethane; crotonic acid and ICl in $CHCl_3$ give at least 92% of *β-chloro-α-iodobutyric acid*, m. p. 64° (converted by boiling pyridine into crotonic and *α-iodocrotonic acid*, m. p. 113°), whilst ethylenesulphonic acid and ICl in aq. HCl furnish at least 90% of $CH_2Cl\cdot CHI\cdot SO_3H$ (converted by neutralisation with K_2CO_3 and evaporation into *K α-iodoethylenesulphonate*). These results and others (lit.) confirm the theory that reaction (addition) is initiated by I.

II. Addition of HI to propylene in presence of propane, $PhNO_2$, AcOH, and H_2O gives in all cases mainly $Pr^\beta I$; the amount of $Pr^\alpha I$ produced decreases for the solvents in the order quoted (when the mol.-fraction of HI present is 0·1). The amount of $Pr^\alpha I$ formed varies (especially in H_2O) with the concentration of HI; curves are given showing the variations. Addition of HBr and HI to Δ^a-pentene in presence of H_2O gives the *sec.*-amyl halides exclusively. In the addition of HX to $CHR{:}CH_2$, orientation is considered to be determined by the electron-repelling effect of R acting both inside and outside the mol., the external effect being affected by the medium. Orientation can be correlated better with the internal pressures than with the dielectric consts. of the media; neither of these factors is, however, accurate.
H. Burton.

Modes of addition to conjugated unsaturated systems. III. Mechanism of addition of halogens and hydrogen halides. C. K. Ingold and H. G. Smith. **IV. Additions of ψ-acids.** J. Bloom and C. K. Ingold (J.C.S., 1931, 2752—2765, 2765—2774).—III. Butadiene and ICl in CH_2Cl_2 at

4 y

−35° give a mixture (*A*) of (mainly) α-chloro-δ-iodo-Δ^β-butene (I) and 22% of γ-chloro-δ-iodo-Δ^α-butene (II); the constitutions of (I) and (II) are established by treatment of *A* with powdered NaOH, addition of 1 mol. of Br to the resultant chlorobutadiene mixture, and ozonolysis of the resulting chlorodibromobutenes. The production of (I) and (II) indicates that the C$_α$-atom is the point of incidence of reaction. β-Methylbutadiene and Br in aq. EtOH give a product which, after treatment with 3% Na–Hg in dil. AcOH, acetylation of the resultant unsaturated alcohols, and oxidation of these with O$_3$ (whereby CH$_2$O, MeCHO, COMe$_2$, α-hydroxy*iso*butaldehyde, and glycollaldehyde are obtained), is calc. to contain at least 47% of CH$_2$Br·CMe:CH·CH$_2$·OH (III), at least 16% of CH$_2$Br·CMe(OH)·CH:CH$_2$ (IV), and a little OH·CH$_2$·CMe:CH·CH$_2$Br (V); the production of (III) and (IV) involves initial reaction at C$_α$, whilst (V) probably results from initial attack at C$_δ$. Addition of Br to α-phenylbutadiene under similar conditions is initiated at C$_δ$, since CHPh:CH·CH(OH)·CH$_2$Br (reduced mainly to γ-phenyl-α-methylallyl alcohol) is formed. αγδ-*Tribromo-Δ^α-butene*, b. p. 114—115°/18 mm. (ozonolysis products, CO, HBr, and α-bromoacraldehyde), is produced from α-bromobutadiene and Br (1 mol.) in hexane at −35°, CHCl$_3$ at +35°, and AcOH at 20°, whilst addition of HBr affords αγ-*dibromo-Δ^α-butene*, b. p. 59—61°/15 mm. (oxidised by KMnO$_4$ in aq. COMe$_2$ to CHMeBr·CO$_2$H). These and other (lit. 1929—1930) results are discussed in relation to the theory previously proposed (A., 1928, 634).

IV. Me malonate and Me β-vinylacrylate give an additive product (cf. Kohler and Butler, A., 1926, 713) (containing less than 2% of the αβ-additive compound) reduced catalytically (Pt-black) in aq. AcOH to *Me pentane-αεε-tricarboxylate*, b. p. 172—176°/19—20 mm., hydrolysed by 20% HCl to pimelic acid. Et cyanoacetate and Et sorbate afford a mixture of Et α-cyano-β-methyl-Δ^γ-pentene-αε-dicarboxylate (VI) and Et α-cyano-β-propenylglutarate (VII) (10±2%). The amount of (VII) is determined by complete hydrolysis of the mixture, subsequent reduction with red P and HI and then with Zn dust and AcOH, dehydration of the mixed acids with Ac$_2$O, and conversion of the resulting β-*n*-propylglutaric anhydride into its anilic acid; multimol. β-methylpimelic anhydride is formed from (VI). Me crotonylidenemalonate and CN·CH$_2$·CO$_2$Me yield a mixture of Me α-cyano-β-methyl-Δ^γ-pentene-αεε-tricarboxylate and Me α-cyano-β-propenylpropane-αγγ-tricarboxylate (16±2%), whilst Et β-*methylsorbate*, b. p. 102—104°/17—18 mm. (cf. A., 1930, 64), and CN·CH$_2$·CO$_2$Et give essentially Et α-cyano-βγ-*dimethyl-Δ^γ-pentene-αε-dicarboxylate*, b. p. 195—200°/15—16 mm., and Et α-methylsorbate and CN·CH$_2$·CO$_2$Et afford mainly Et α-cyano-αε-*dimethyl-Δ^γ-pentene-αε-dicarboxylate*, b. p. 196—200°/17—18 mm.; the amount of αβ-addition in the last two cases is not more than 2%. The additive product from Me malonate and Me cinnamylideneacetate is wholly αβ, since successive hydrolysis, decarboxylation, and ozonolysis give BzOH and tricarballylic acid. The reaction between Me cinnamylidenemalonate and CN·CH$_2$·CO$_2$Me is initiated by αβ-addition, since *Me*

α-*cyanocinnamylideneacetate*, m. p. 143—145° (from cinnamaldehyde and CN·CH$_2$·CO$_2$Me), and Me malonate are produced. These results and others (lit. 1930—1931) are discussed with reference to the theory previously proposed (*loc. cit.*), which is now amplified.

Ph styryl ketone, CH$_2$Br·CO$_2$Et, and Zn in C$_6$H$_6$ give Et β-*hydroxy-β-phenyl-β-styrylpropionate*, m. p. 93°, dehydrated to Et β-*styrylcinnamate*, b. p. 237°/10 mm. (free *acid*, m. p. 145°, converted by Br in CHCl$_3$ into a *Br*-derivative, m. p. 170°), which could not be combined with CN·CH$_2$·CO$_2$Et in presence of NaOEt. p-*Bromobenzyl cyanoacetate*, m. p. 84—85° (from p-Br·C$_6$H$_4$·CH$_2$Br and CN·CH$_2$·CO$_2$Ag), and *Me* γ-*benzoyl-β-phenylpropane-αα-dicarboxylate*, m. p. 104° (from Ph styryl ketone and Me malonate in presence of piperidine), are described.

H. BURTON.

Pentene derivatives. R. PAUL (Compt. rend., 1931, **193**, 598—600).—Δ^δ-Pentenol with NPhMe$_2$ and SOCl$_2$ gives Δ^δ-*pentenol chloride* (I), b. p. 105°/745 mm., with PBr$_3$ and a little pyridine Δ^δ-*pentenyl bromide* (II), b. p. 126—127°/765 mm., and with Ac$_2$O yields Δ^α-pentenyl acetate, b. p. 150—151° (αβ-*dibromoamyl acetate*, b. p. 156—157°/23 mm.). δε-Dibromo-*n*-amyl alcohol with solid KOH gives 2-bromomethyltetrahydrofuran and δ-*bromo-Δ^δ-pentenyl alcohol*, b. p. 97°/15 mm.; this with PBr$_3$ and dry pyridine yields αδ-*dibromo-Δ^δ-pentene*, b. p. 83—86°/15 mm., and with KOAc δ-*bromo-Δ^δ-pentenyl acetate*, b. p. 102—105°/18 mm. The difference in the physical consts. of succeeding members of the series CH$_2$:CH·[CH$_2$]$_n$·CH$_2$X decreases as *n* increases. (I) and (II) react normally with Mg.   R. S. CAHN.

Photochemical oxidation of acetylene. R. LIVINGSTON.—See this vol., 1379.

Stability of hexa*tert.*-alkylethinylethanes. Effect of increasing the weight of the alkyl groups. D. W. DAVIS and C. S. MARVEL (J. Amer. Chem. Soc., 1931, **53**, 3840—3851).—γδ-Dimethylhexane-γδ-diol is converted by Nybergh's method (A., 1922, i, 802) into Me α-methyl-α-ethylpropyl ketone (admixed with a little Et *tert.*-amyl ketone), which with PCl$_5$ gives impure β-chloro-γ-methyl-γ-ethyl-Δ^α-pentene. Treatment of this with NaNH$_2$ in high-boiling mineral oil at 160—175° (whereby some δδ-dimethyl-Δ^β-hexinene is evolved) and subsequent hydrolysis affords γ-*methyl-γ-ethyl-Δ^α-pentinene*, b. p. 98—100°/745 mm. [*Ag salt*, m. p. 191·5° (darkens at 167°)], converted by the method previously described (A., 1928, 988) into *tri-(γ-methyl-γ-ethyl-Δ^α-pentinyl)carbinol*, b. p. 130—133°/0·5 mm. The corresponding bromide (from the carbinol and AcBr in light petroleum) and "mol." Ag in Et$_2$O and N$_2$ give *hexa-(γ-methyl-γ-ethyl-Δ^α-pentinyl)ethane* (I), m. p. 122—127° according to rate of heating, m. p. (Maquenne block) 195°. (I) in EtOH absorbs O$_2$ readily, but a peroxide could not be isolated; CO$_2$ and α-methyl-α-ethylbutyric acid (p-*toluidide*, m. p. 113·5—114°) are formed. (I) is cleaved readily by liquid Na–K alloy or 40% Na–Hg in Et$_2$O; the resultant products with CO$_2$ give *tri-(γ-methyl-γ-ethyl-Δ^α-pentinyl)acetic acid*, m. p. 171—174° (corr.). (I) is cleaved more readily with 1% Na–Hg than is hexa*tert.*-butylethinylethane (*loc. cit.*);

the decreased stability of the central C·C linking is attributed to the increase in wt. of the alkyl groups. When (I) is heated in EtOH and N_2 an *isomeride*, m. p. 82·3—83° (corr.), is produced. H. BURTON.

Determination of organic halogen by liquid ammonia–sodium process. T. H. VAUGHN and J. A. NIEUWLAND (Ind. Eng. Chem. [Anal.], 1931, 3, 274—275).—A simple modification of the method of Chablay (A., 1914, i, 918), which is also applicable to the determination of F in org. compounds.

H. BURTON.

Addition of hydrogen bromide to vinyl bromide. J. P. WIBAUT (Rec. trav. chim., 1931, 50, 1021—1022; cf. this vol., 598).—A reply to Burkhardt and Cocker (this vol., 1031). J. W. BAKER.

Resolution of unsaturated asymmetric alcohols into optically active isomerides. G. KAMAI (J. Gen. Chem. Russ., 1931, 1, 460—466).—Ethylvinyl-carbinol can be resolved through its *H phthalate*, m. p. 121—124° (*benzylamine* salt, m. p. 102°; *brucine* salt, m. p. 143—144°). *Brucine β-methylenebutyl phthalate*, m. p. 85—86°, was synthesised in order to show that during the formation of the former brucine salt no rearrangement had taken place. Phenylvinylcarbinol is not resolvable by this method, as the action of phthalic anhydride gives *cinnamyl H phthalate*, m. p. 88—89°. The following new compounds are described: d-*ethylvinylcarbinyl H phthalate* (*benzylamine* salt, m. p. 89—90°), d-*ethylvinylcarbinol*, b. p. 110—112°, l-*phenylethylammonium ethylvinylcarbinyl phthalate*, m. p. 142—142·5°, l-*ethylvinylcarbinol*, b. p. 111—112°. E. B. UVAROV.

Determination of acetylenic alcohols and the composition of their silver compounds. W. KRESTINSKI and M. KELBOVSKAJA (Ber., 1931, 64, [B], 2371—2375).—Treatment of γ-ethyl-Δ^α-pentinen-γ-ol, γ-methyl-Δ^α-pentinen-γ-ol, and δ-methyl-Δ^α-pentinen-γ-ol with AgOAc ppts. *Ag* salts 2XAg,AgOAc, reaction being of the type 2OH·CEt$_2$·C:CH + 3AgOAc = 2OH·CEt$_2$·C:CAg,AgOAc + 2AcOH. After removal of the ppt. the alcohol is determined by titration of the acid with NaOH in presence of phenolphthalein. γ-Methyl-Δ^α-butinen-γ-ol and Δ^α-butinen-γ-ol do not give ppts. with AgOAc or Ag propionate. With saturated Ag *iso*butyrate, the *ppts.* have the compositions OH·CMe$_2$·C:CAg,C$_4$H$_7$O$_2$Ag and OH·CHMe·C:CAg,C$_4$H$_7$O$_2$Ag; titration of the *iso*butyric acid in the filtrates from these ppts. is not a satisfactory method for determining the alcohols. H. WREN.

Reaction of pentaerythritol with aldehydes under the influence of zinc chloride. H. J. BACKER and H. B. J. SCHURINK (Rec. trav. chim., 1931, 50, 1066—1068).—*spiro*Cyclic acetals of the type $C\left(<\!\!\begin{array}{c}CH_2 \cdot O\\CH_2 \cdot O\end{array}\!\!>CR^1R^2\right)_2$ are readily prepared by warming C(CH$_2$·OH)$_4$ with 20—25% excess of the appropriate aldehyde in presence of a little anhyd. ZnCl$_2$, and thus are obtained: *di*-(β-*tribromoethyl-idene*)- (R^1=H; R^2=CBr$_3$), m. p. 248—249° (decomp.), and *difurfurylidene*- (R^1=H; R^2=C$_4$H$_3$O), m. p. 164·5—165°, -*pentaerythritol*. With *cyclo*pentanone and *cyclo*hexanone the tetracyclic trispirans *di*(*cyclo*-pentylidene)- [R^{1}R^2=(CH$_2$)$_4$>], m. p. 153·5°, and

di(*cyclo*hexylidene)- [R^{1}R^2=(CH$_2$)$_5$>], m. p. 115·5°, -*pentaerythritol*, are obtained. With α-hydrindone the C(CH$_2$·OH)$_4$ plays no part in the reaction, the products being α-anhydrobishydrindone and truxene.

J. W. BAKER.

Action of chloroformic esters on alkylsul-phuric acids. M. Y. KRAFT and F. V. LIUTINA (J. Gen. Chem. Russ., 1931, 1, 190—192).—The reaction RHSO$_4$+ClCO$_2$R′=RR′SO$_4$+CO$_2$+HCl proceeds smoothly when R and R′ are Et or Me. The reaction is recommended for the prep. of Me$_2$SO$_4$.

E. B. UVAROV.

α- and β-Glycerophosphates. P. KARRER and H. SALOMON (J. Biol. Chem., 1931, 93, 407).—Polemical (cf. Kay and Lee, this vol., 766). H. BURTON.

α- and β-Glycerophosphates. H. D. KAY (J. Biol. Chem., 1931, 93, 409).—A reply to Karrer and Salomon (preceding abstract). H. BURTON.

Synthesis of galactose 6-phosphate. B. HVIS-TENDAHL (Svensk Kem. Tidskr., 1931, 43, 202—205; cf. A., 1930, 1166).—*Ba diisopropylidenegalactose 6-phosphate*, C$_{12}$H$_{19}$O$_9$PBa, $[\alpha]_{Hg\ yellow}^{20}$ —27·8° in H$_2$O, has been prepared from diisopropylidene-galactose and POCl$_3$ in pyridine solution. This compound is hydrolysed to *Ba galactosephosphate*, C$_6$H$_{11}$O$_9$PBa, $[\alpha]_{Hg\ yellow}^{20}$ +21° in H$_2$O. The ester obtained by treatment of the Ba compound with the calc. amount of H$_2$SO$_4$ has $[\alpha]_{Hg\ yellow}^{20}$ +31°.

H. F. HARWOOD.

Thermal behaviour of sulphur compounds in hydrocarbon solvents. I. Aliphatic mercaptans. W. M. MALISOFF and E. M. MARKS (Ind. Eng. Chem., 1931, 23, 1114—1120).—Experiments on the thermal decomp. of mercaptans in org. solvents are reproducible in calibrated furnaces. Below 475°, C$_6$H$_6$, *n*-heptane, βββ-trimethylpentane, and straight-run naphthas are sufficiently stable to serve as solvents which do not react with mercaptans or their decomp. products. The AgNO$_3$ method has been adapted for the determination of mercaptans in mixtures containing the thermal decomp. products, giving an accuracy of ±5 to ±2%. Decomp. of the aliphatic mercaptans is homogeneous in the gaseous phase up to 475°. The decomp. of amyl mercaptan is depressed by mixing with CO$_2$ or H$_2$, but is promoted by C$_6$H$_6$, in relation to naphtha as solvent, but the contrary is true for aromatic types. The data suggest a first-order reaction, although a final decision is not possible. The decomp. of the aliphatic types is apparently to H$_2$S and an olefine. The higher homologues in the aliphatic series appear to be more unstable than the lower, although there is no marked difference. Benzyl mercaptan is less stable than the lower members of the aliphatic series. Branched-chain isomerides are less stable than the straight-chain compounds, markedly so only at 475°. Some activation of decomp. may be attributed to a solvent such as C$_6$H$_6$ compared with naphtha as standard, but naphtha itself may be a promoter. The temp. coeff. for a rise of 10° is calc. to be 1·38 for *n*-amyl mercaptan, with a heat of activation of 33,500 g.-cal. The val. of E/RT is 24·7, of the same order of magnitude as those calc. for the decomp. of NH$_2$Et, O$_3$, N$_2$O$_5$. COMe$_2$, and Et$_2$O. E. S. HEDGES.

Reaction of silver nitrate with organic sulphides. P. C. Rây, N. Adhikari, and H. Rây (J. Indian Chem. Soc., 1931, 8, 689—693).—Unstable additive (1 : 1) *compounds* (m. p. given in parentheses) are obtained from a conc. solution of AgNO₃ and the following sulphides : Me₂S (126°), Et₂S (112°), Pr₂S (109°), Bu₂S (98°), MeEtS, (CH₂Ph)₂S (93—95°), Me₂S₂, Et₂S₂, and (CH₂Ph)₂S₂ (103°); allyl sulphide gives the *compound* 3AgNO₃,2(C₃H₅)₂S, m. p. 152°. These compounds are binary electrolytes and are decomposed by pyridine and NH₃ to AgNO₃,2C₅H₅N and AgNO₃,2NH₃, respectively. The *complexes* Hg(NO₂)₂,2Me₂S, HgClNO₃,Et₂S, m. p. 110°, HgClNO₃,Pr₂S, m. p. 100—102°, and HgClNO₃,Bu₂S, m. p. 132°, are obtained when the AgNO₃,R₂S compounds are treated with HgCl₂ in EtOH.

H. Burton.

Complexes of antimony trichloride with organic sulphides. P. C. Rây, N. Adhikari, and A. N. Roy (J. Indian Chem. Soc., 1931, 8, 711—716). —The following *complexes* are obtained when the components are heated at 120—190° : SbCl₃,Et₂S (I), m. p. 143°; SbCl₃,Me₂S; SbCl₃,Pr₂S, m. p. 124°; 4SbCl₃,3Bu₂S (II), m. p. 105°. (I) and (II) are converted by warm EtOH into the *complexes* 2SbCl₃,HCl,3Et₂S, m. p. 75°, and 2SbCl₃,HCl,3Bu₂S, m. p. 125°, respectively; (I) and HgCl₂ in COMe₂ give the *compound* Hg₂Cl₂,Et₂S. (I) is decomposed by AgNO₃ and NH₃ to Sb₂S₃. The conductivity of (I) in COMe₂ is greater than that of SbCl₃ under the same conditions.

H. Burton.

Reactions of divinyl sulphide, sulphoxide, and sulphone. J. R. Alexander and H. McCombie (J.C.S., 1931, 1913—1918).—Divinyl sulphide and Cl₂ (1 mol.) in CCl₄ affords αβ-*dichloroethyl vinyl sulphide*, b. p. 84—85°/20 mm. (converted by KOH in EtOH into β-*chlorodivinyl sulphide*, b. p. 123—124°/760 mm.), whilst with 2 mols. of Cl₂ αβα'β'-*tetrachlorodiethyl sulphide*, b. p. 132—133°/15 mm., converted by NEt₃ (1 mol.) in C₆H₆ into αβ-*dichloroethyl β'-chlorovinyl sulphide*, b. p. 103—104°/20 mm., is obtained. Similar addition of PhSH gives di-β-phenylthioldiethyl sulphide. Divinyl sulphoxide (by NEt₃ on ββ'-di-iododiethyl sulphoxide in dry C₆H₆) forms no additive compounds with hydrogen halides, but by addition of the appropriate halogen are obtained : αβα'β'-*tetrachloro-*, m. p. 121°, and -*tetrabromo-*, m. p. 119°, -*diethyl sulphoxide*, whilst 5% NaOH converts it into 1 : 4-thioxan oxide, and NaOR in ROH gives the corresponding ββ'-dialkoxydiethyl sulphoxide. β-*Chlorodivinyl sulphoxide*, b. p. 73—74°/15 mm., is obtained by the action of NEt₃ on trichlorodiethyl sulphoxide. Divinyl sulphone (by NEt₃ on ββ'-dichlorodiethyl sulphone in dry C₆H₆) is very reactive, suitable addition of halogens or hydrogen halides giving αβα'β'-*tetrabromodiethyl sulphone*, m. p. 138°, ββ'-dibromodiethyl sulphone (no reaction with Cl₂ or HCl), and β-chloroethyl vinyl sulphone (NEt₃ on the dichloro-sulphone), converted by aq. HI into β-*chloro-β'-iododiethyl sulphone*, m. p. 125—126° (decomp.) ; ββ'-*dicyanodiethyl sulphone* has m. p. 84°. With 5% NaOH divinyl sulphone gives 1 : 4-thioxan dioxide, whilst NaOMe in boiling McOH affords ββ'-*dimethoxydiethyl sulphone*, b. p. 170—171°/17 mm., the

diethoxy- and di*iso*amyloxy-compounds being obtained similarly ; NH₂Ph at 100° affords ββ'-*dianilinodiethyl sulphone*, m. p. 94—95°, glycine ester in EtOH gives Et 1 : 4-sulphonazan-4-acetate, whilst with NHPh·NH₂, 4-anilino-1 : 4-sulphonazan, NHPh·N<(CH₂·CH₂)₂>SO₂, m. p. 192°, is obtained. Divinyl sulphone with H₂S gives mainly polymerisation products and a small yield of 1 : 4-*dithian dioxide*, SO₂<(CH₂·CH₂)₂>S, m. p. 206°.   J. W. Baker.

Salts of methanetrisulphonic acid. H. J. Backer and P. Terpstra (Rec. trav. chim., 1931, 50, 1069—1077).—Crystallographic data are given for the following salts of CH(SO₃H)₃+3H₂O, m. p. 162—162·5° (cf. this vol., 64) : NH₄+0·5H₂O; *Li*+4H₂O; *Na*+3H₂O; *Rb*+H₂O (mixed crystals with K salt); *Cs*+H₂O; and +2H₂O; Ag+H₂O; *Ca*+12H₂O; *Ba*+9H₂O; La+6H₂O; *cinchonine*+8H₂O; and *K dibrucine* +9H₂O.   J. W. Baker.

Trisulphonylmethanes. D. T. Gibson (J.C.S., 1931, 2637—2644).—Disulphonylmethanes are prepared either by Posner's method (A., 1903, i, 242) or by successive hydrolysis and oxidation of sulphonyl-thiolacetones (I), SR'·CHAc·SO₂R, obtained by condensation of sulphonylacetones and alkyl thiosulphonates (cf. Brooker and Smiles, A., 1926, 947): CH₂Ac·SO₂R+R·SO₂·SR'—→(I). Condensation of the disulphonylmethanes with disulphoxides in presence of NaOEt or Na₂CO₃ gives disulphonylthiolmethanes, oxidised further to trisulphonylmethanes, CH(SO₂R)(SO₂R')(SO₂R''), which could not be resolved. The following are prepared : CH₂(SO₂Me)₂, m. p. 142° (*Cl₂*-derivative, m. p. 152°); αα-*dimethylthiolethane*, b. p. 156—158°; αα-*di(methanesulphonyl)-ethane*, m. p. 122° (*I*-derivative, m. p. 225°); *methylthiolethylthiolmethane*, b. p. 163—167°; *methanesulphonylethanesulphonylmethane*, m. p. 94—95°; *phenylthiolethylthiolmethane*, b. p. 147—151°; CH₂(SO₂Ph)(SO₂Et) [also formed by oxidising the reaction product from Et *p*-toluenethiosulphonate and Et benzenesulphonylacetate (*Na* salt)]; α-*phenylthiol-α-methylthiolethane*, b. p. 140—145°/10 mm.; α-*benzenesulphonyl-α-methanesulphonylethane*, m. p. 104°; *phenylthiolmethylthiolmethane*, b. p. 148—152°/11 mm.; *benzenesulphonylmethanesulphonylmethane*, m. p. 147°; α-*benzenesulphonyl-α-p-tolylthiolacetone*, m. p. 99°; *benzenesulphonyl-p-tolylthiolmethane*, m. p. 85°; *benzenesulphonyl - p-toluenesulphonylmethane*, m. p. 115°; *methanesulphonylethanesulphonylphenylthiolmethane*, m. p. 126°; *benzenesulphonylethanesulphonylmethylthiolmethane*, m. p. 98°; *benzenesulphonylmethanesulphonylethanesulphonylmethane*, m. p. 216—219° [*Br*-derivative, m. p. 141°; *brucine*, m. p. 140—150° (decomp.), and d-*hydroxyhydrindamine*, m. p. 159°, salts]; *benzenesulphonyl-p-toluenesulphonyl-3 : 5-dichlorophenylthiolmethane*, m. p. 145° (sinters at 123°); *benzenesulphonyl-p-toluenesulphonylmethylthiolmethane*, m. p. 105°; *benzenesulphonylmethanesulphonyl-p-tolylthiolmethane*, m. p. 169°; *benzenesulphonyl-p-toluenesulphonylmethanesulphonylmethane*, m. p. 174°; *benzenesulphonylmethanesulphonyl - 3 : 5 - dichloro-phenylthiolmethane*, m. p. 147°, and *benzenesulphonyl-3 : 5-dichlorobenzenesulphonylmethanesulphonylmethane*, m. p. 208° (becoming blue). CH₂(SO₂Et)₂ and

Ph·SO$_2$Cl give *chlorodi(ethanesulphonyl)methane*, m. p. 96°. *Me* p-*toluenethiosulphonate*, m. p. 58°, and benzenesulphonylacetone afford a *compound*, $C_{11}H_{14}O_3S_2$, m. p. 77°, hydrolysed to a *substance*, $C_9H_{12}O_2S_2$, m. p. 80°, which is oxidised to p-*toluenesulphonylmethanesulphonylmethane*, m. p. 158°.

Halogen (X) in compounds containing the ·SO$_2$·CX$_2$·SO$_2$· group is readily determined by dissolving the compound in warm alkaline sulphite solution and subsequent precipitation as AgX. The method works well with 2 : 2-*dichloro-*, m. p. 233°, and 2-*bromo-2-methyl-*, m. p. 248°, -1 : 3-*dithiolan dioxides* and with the Br_4 derivative, m. p. 205°, of *methyl-* 1 : 3 : 5-*trithian* 1′ : 3-*dioxide* (from the trithian dioxide and Me$_2$SO$_4$ in the cold).   H. BURTON.

Sodium ethane-αβ-disulphonate. H. J. BACKER and P. TERPSTRA (Rec. trav. chim., 1931, **50**, 1078—1081).—Contrary to various data in the literature this salt exists in only two forms, +2H$_2$O (prisms or pseudo-octahedra) and +3H$_2$O (thin plates), crystallographic data for which are given.   J. W. BAKER.

Determination of organic acids. V. Application of partition method to determination of acetic, propionic, and butyric acids in mixture. O. L. OSBURN and C. H. WERKMAN (Ind. Eng. Chem. [Anal.], 1931, **3**, 264—265).—The amount of each acid in an aq. solution of the mixture is determined from the percentage partition coeffs. (A., 1930, 1161) of the mixture (adjusted to 0·08—0·12N) with two different amounts of Pr$^\beta_2$O.   H. BURTON.

Ring–chain tautomerism of partly acetylated, polyhydric alcohols. H. MEERWEIN and H. SÖNKE (Ber., 1931, **64**, [*B*], 2375—2381; cf. this vol., 206).—The resistance towards alkali and ready hydrolysis by dil. acid of the compound obtained by the action of diazomethane on β-hydroxyethyl trichloroacetate is explained by assuming it to be *Me ethylene trichloro-orthoacetate*, CCl$_3$·C(OMe)$\begin{smallmatrix}O·CH_2\\O·CH_2\end{smallmatrix}$. This view is supported by its non-identity with β-*methoxyethyl trichloroacetate*, b. p. 92—93°/10 mm., m. p. 14·6—14·8°, prepared from CCl$_3$·COCl and β-methoxyethyl alcohol and readily converted by cold H$_2$O into CCl$_3$·CO$_2$H and glycol Me ether; further, treatment of Me ethylene trichloro-orthoacetate with Pr^{a}OH and HCl affords *Pr^a ethylene trichloro-orthoacetate*, b. p. 128—130°/12 mm. The possible tautomerism of β-hydroxyethyl trichloroacetate is thus established, whilst its ready hydrolysis by cold H$_2$O or dil. NaOH and its conversion by NH$_3$ into CCl$_3$·CO·NH$_2$ and ethylene glycol are evidence of acyclic structure. Similarly, with AcCl it gives smoothly β-*acetoxyethyl trichloroacetate*, b. p. 122°/11 mm., quantitatively converted by cold H$_2$O or dil. alkali into CCl$_3$·CO$_2$H and β-hydroxyethyl acetate and prepared also from CCl$_3$·COCl and β-hydroxyethyl acetate. With SOCl$_2$ it affords exclusively β-*chloroethyl trichloroacetate*, b. p. 97°/10 mm., prepared also from CCl$_3$·COCl and ethylene chlorohydrin.

The work of Hibbert and Greig (this vol., 820) is criticised.   H. WREN.

Preparation of *n*-decoic acid. C. H. KAO and S. MA (J.C.S., 1931, 2046—2047).—Bromination of lauryl chloride (by SOCl$_2$ on the acid) and subsequent treatment with the appropriate alcohol afford the following esters of α-bromolauric acid : *Me*, b. p. 135—137°/3 mm.; *Et*, b. p. 144—146°/3 mm.; *Pr$^\beta$*, b. p. 146—148°/3 mm.; *Pr^a*, b. p. 149—151°/3 mm.; *Bu$^\beta$*, b. p. 152—154°/3 mm.; *Bu^a*, b. p. 154—156°/3 mm.; and iso*amyl*, b. p. 158—160°/3 mm. Hydrolysis of these with KOH in EtOH affords Δ^a-dodecenoic acid (*amide*, m. p.112·5—113·5°; p-*toluidide*, m. p. 85—86°), which, when heated with moist KOH at 300°, readily affords *n*-decoic acid in good yield.   J. W. BAKER.

Oxidation of unsaturated fatty acids. I. Oxidation of highly purified oleic acid by gaseous oxygen with and without catalysts. J. H. SKELLON (J.S.C.I., 1931, **50**, 382—386T).—When oleic acid was oxidised at 100° by O$_2$ without catalyst a tenfold increase in the percentage of "oxidised acids" recorded by earlier workers was obtained. The following were also produced : ικ-dihydroxy-stearic acid, m. p. 132°, crude nonoic acid, a mixture containing hydroxylated acids and *iso*oleic acid, and traces of HCO$_2$H and AcOH.

Oxidation of oleic acid at 120° in presence of a trace of "blown" whale oil as catalyst yielded ικ-dihydroxystearic acids of m. p. 132° and 95°, small percentages of azelaic acid and κ-hydroxystearic acid, m. p. 84°, crude hydroxylated acids (equiv. 313—319), a mixture containing *iso*oleic acid, traces of formic, acetic, and oxalic acids, and MeCHO. Rupture of the carbon chain had not occurred in 15 hr.; quant. yields of scission products were not obtained.

Isomerism of linoleic acid. I. G. V. PIGULEVSKI and A. Y. VASILIEV (J. Gen. Chem. Russ., 1931, **1**, 235—239).—Oxidation of Me linoleate gives two isomeric *Me dihydroxylinoleates* in equal quantities : solid, m. p. 32°, and a liquid. These give the corresponding *dihydroxylinoleic acids*, solid, m. p. 78°, and a liquid. Hydrolysis of the solid gives tetrahydroxy-stearic acid, not given by the liquid isomeride.   E. B. UVAROV.

Composition of linseed oil. H. VAN DER VEEN (Chem. Umschau, 1931, **38**, 277—279).—A reply to Kaufmann and Keller (cf. this vol., 1034). Purification of the linoleic–linolenic acid mixture through the Li salts is questioned : this method might conceivably separate existing stereoisomerides.   E. LEWKOWITSCH.

Composition of linseed oil. J. VAN LOON (Chem. Umschau, 1931, **38**, 279—281).—A reply to Kaufmann and Keller (this vol., 1035). The reaction time in the determination of CNS val. may safely be prolonged to 3 days : the linseed oil in question had an abnormally high CNS val. The CNS val. of Et linolenate indicates the probable presence of isomerides of different reactivity. The CNS val. of *Picramnia* fat (containing ε-stearolic acid) increases with the reaction time even with great excess of reagent (cf. B., 1931, 400).   E. LEWKOWITSCH.

Synthesis of fatty acids of high mol. wt. and of their anhydrides. W. BLEYBERG and H. ULRICH (Ber., 1931, **64**, [*B*], 2504—2513).—The prep. of fatty acids along the lines R·CO$_2$H⟶R·CO$_2$Et⟶

$R\cdot CH_2\cdot OH \longrightarrow R\cdot CH_2I \longrightarrow R\cdot CH_2\cdot CH(CO_2Et)_2 \longrightarrow$ $R\cdot CH_2\cdot CH(CO_2H)_2 \longrightarrow R\cdot CH_2\cdot CH_2\cdot CO_2H$ is dissected. The difficulties in the reduction of ester to alcohol by Na and EtOH, due to hydrolysis of the ester, are overcome by dissolving the ester in light petroleum, b. p. 30—50° or 70—80°, containing an excess of Na wire and gradually adding the necessary amount of EtOH. After prolonged boiling, excess of 96% EtOH is added and the solution is boiled to hydrolyse residual ester. Bimol. products [glycols, acyloins, or diketones) are produced in only minor amount; the alcohols are therefore best purified by distillation in high vac. Difficulties encountered in applying this procedure to the higher esters (e.g., Et behenate) are avoided by replacing EtOH by BuOH. In the malonic ester condensation EtOH is advantageously replaced by BuOH, since Et sodiomalonate dissolves readily in the last-named substance and the reaction with the sluggish iodides can be effected at a higher temp. Formation of ketones during the decomp. of the substituted malonic acids is avoided by conducting the operation at 140—150° at first in the vac. of a water pump and finally in high vac. and subsequent immediate distillation of the fatty acid in high vac. The transition from stearic to n-eicosoic acid is thus effected with an over-all yield of 77·4%. It appears characteristic of individual acids that they solidify from the molten state with a coarsely cryst. surface and loose texture, whereas mixtures of them have a microcryst. structure and are comparatively compact. Anhydrisation of the acids is effected by repeated treatment with Ac_2O and intermediate distillation, finally in high vac., of AcOH and excess of Ac_2O, after which the anhydrides are crystallised from light petroleum. The following data are recorded : arachidic acid, m. p. 76·1—76·3° (anhydride, m. p. 77·5—77·7°); behenic acid, m. p. 80·3—80·7° (anhydride, m. p. 81·7—81·9°; Et ester, m. p. 48·0— 48·5°; behenyl alcohol, m. p. 70·0—70·5°, and iodide, m. p. 47·5—48·0°); lignoceric acid, m. p. 84·5—84·9° (anhydride, m. p. 86·0—86·3°; Et ester, m. p. 54·5— 55·0°; lignoceryl alcohol, m. p. 75·2—75·5°, and iodide, m. p. 53·4—53·8°); cerotic acid, m. p. 87·7— 87·9° (anhydride, m. p. 89·3—895°; Et ester, m. p. 59·5—59·8°; cerotyl alcohol, m. p. 79·3—79·6°, and iodide, m. p. 58·2—58·5°); eicosanoctoic acid, m. p. 90·3—90·5° (anhydride, m. p. 92·7—92·9°; Et ester, m. p. 59·5—59·8°; eicosanoctyl alcohol, m. p. 79·3— 79·6°, and iodide, m. p. 62·8—63·2°); melissic acid, m. p. 91·9—92·1°.　　　　　　　　　H. WREN.

Constituents of petroleum. I. J. VON BRAUN [with R. DEUSER, A. HEYMONS, L. MANNES, W. MAY, M. REUTER, E. ANTON, W. KELLER, E. FRIEHMELT, and O. SCHORNING] (Annalen, 1931, **490**, 100—179).— The naphthenic acids from various sources are separated into definite fractions by lengthy processes of fractional distillation of them and their esters; complete separation from accompanying hydrocarbons and phenols is difficult. They are best characterised by conversion into the amine with 1 C less by action of dry N_3H in H_2SO_4 which gives yields of the order of 90%, whereas the yields by Hofmann's method are very poor in this field; the amines are more readily separated than the acids

by distillation, and are finally purified by crystallisation of their oxalates, by which means products of definite empirical composition, nevertheless consisting of mixtures of isomerides, are obtained. The following tests of structure are applied to the acids : (1) chlorination of their ethylamides (cf. A., 1927, 547) whereby a distinction is made between primary, sec., and tert. bound CO_2H groups; attempts at oxidation of the Cl_2-acids to the next lower failed; (2) bromination by the Hell–Volhard–Zelinski method, removal of HBr from the bromo-ester by a tert.-amine, isomerisation of the αβ- to the βγ-acid and lactonisation of the latter by conc. H_2SO_4, and oxidation of the lactone; formation of succinic acid indicates the structure $R\cdot[CH_2]_3\cdot CO_2H$ in the original acid; (3) the alcohol produced by Na–EtOH reduction of the Et ester is converted into its bromide, which is combined with NMe_3, and the corresponding base distilled with conc. aq. KOH, and the olefine produced ozonised to the aldehyde, which on oxidation gives the next lower homologue of the original acid; (4) the amine (N_3H) is converted into its methiodide and the derived quaternary base treated as in (3); a ketone is thus produced from acids of the type $R\dot{:}CH\cdot CH_2\cdot CO_2H$, and an acid from the type $R'\cdot CH_2\cdot CH_2\cdot CO_2H$.

The modified Hofmann degradation used in (3) and (4) lessens the extremely marked tendency of the higher ammonium hydroxides to split off MeOH and regenerate the original amine (cf. A., 1927, 650); nevertheless this is still the principal reaction in many cases, and the process of forming the quaternary base and submitting it to decomp. often needs to be repeated more than once. This may lead to the fractionation of isomeric mixtures; thus the fraction $C_9H_{16}O_2$, b. p. 139—141°/12 mm., from Rumanian petroleum was converted by method (3) into the acid $C_8H_{14}O_2$, which was then converted into the amine (N_3H), the metho-hydroxide of which was distilled with KOH; the fraction that resisted decomp. appeared to be a chemical individual $C_5H_{10}\dot{:}CH\cdot CH_2\cdot NMe_2$, b. p. 163° (picrate, m. p. 138— 141°, sinters 136°; methiodide, m. p. 213—215°).

Various qualities of distilled, and one of crude, Rumanian petroleum, and also oils from California (distilled), Germany (crude), and Galicia (distilled) were examined. The naphthenic acids from all these sources had the same general characteristics; they belonged to the aliphatic (paraffin) class up to C_{6-7}, monocyclic from C_7 to C_{12}, and to the dicyclic series above C_{12} (at least to C_{22}, there being no definite evidence of the occurrence of more highly condensed systems). Acids of approx. the same empirical composition occur in corresponding fractions of the products from these widely differing sources. Among the distilled oils the Galician oil alone formed an exception to the above generalisations, and contained only aliphatic and monocyclic (above C_{11}) acids. In crude Rumanian oil the lower members, found in the distilled oils, are absent and more sec.-acids are present, suggesting that the lower members are the products of pyrogenic decomp. during refining.

From the fraction $C_{10}H_{18}O_2$, b. p. 148—155°/12 mm., from Rumanian oil, and corresponding fractions from Galician and Californian oils, a ketone, $C_8H_{14}O$,

b. p. 172—174° (*semicarbazone*, m. p. 163°; *di-p-nitrobenzylidene* derivative, m. p. 188—190°), was isolated by method (4); acids were also present in the first two oils that gave succinic acid by method (2). The ketone is concluded to be 3 : 3 : 4-*trimethyl-cyclopentanone*, since, like all the other ketones isolated, it gave no evidence of the presence of a COMe group, and it is different from all the possible *cyclopentanone* isomerides (cf. this vol., 1417). A mixture of monocyclic, $C_{11}H_{21}\cdot NH_2$, and dicyclic, $C_{13}H_{23}\cdot NH_2$, amines was obtained from the acids, b. p. 183—200°/12 mm., from the heavier Rumanian oils by action of N_3H; by method (4) the former is converted into a *ketone*, $C_{10}H_{18}O$, b. p. 201—204° (*semicarbazone*, m. p. 162°), identical with that from a similar fraction (b. p. 162—173°/16 mm.) from Californian oil, and the latter into a dicyclic *ketone*, $C_{11}H_{18}O$, b. p. 230—234° (*semicarbazone*, m. p. 169°; *oxime*, b. p. 155°/14 mm.). The next higher fraction from Californian oil gives by similar methods the *ketone*, $C_{12}H_{20}O$, b. p. 255—260° (*semicarbazone*, m. p. 162°).

Cyclic ureides, apparently individual substances, were isolated from two fractions by reduction to the alcohol, conversion into the bromide, condensation of the bromide with Et sodiomalonate, and treatment of the resulting ester with carbamide and NaOEt in EtOH. The *ureide*, $C_{14}H_{22}O_3N_2$, m. p. 230° [β-*bromo-allyl* derivative, m. p. 144—154° (from crude ureide)], from the fraction b. p. 148—155°/12 mm., and the *ureide*, m. p. 220°, from the fraction b. p. 190—210°/12 mm., both of Rumanian origin, are described. Campholic and fencholic acids readily give the corresponding amines (NH_2 replaces CO_2H) on treatment in conc. H_2SO_4 with N_3H in C_6H_6 or $CHCl_3$. The Cl_2-derivative, m. p. 47—48°, of *stearmethyl-amide*, m. p. 77—79°, b. p. 185°/0·2 mm., is hydrolysed by 90% aq. $PhSO_3H$ at 140—150° to dichloro-stearic acid (*anilide*, m. p. 41—45°), but attempts to oxidise this to margaric acid by a variety of agents failed. H. A. PIGGOTT.

Structure of enol-acetates and the corresponding vinylamines. L. J. ROLL and R. ADAMS.—See this vol., 1419.

Lævulic acid. III. Hydrogenation of alkyl esters in presence of platinum catalyst. R. W. THOMAS, H. A. SCHUETTE, and M. A. COWLEY (J. Amer. Chem. Soc., 1931, 53, 3861—3864).—The rate of catalytic reduction (Adams) of alkyl (Me, Et, Pr, Pr$^\beta$, Bu, Bu$^\beta$) lævulates in absence or presence of Et_2O at 22—24° varies inversely with the size of the alkyl group; the Pr (Bu) ester is reduced more rapidly than the Pr$^\beta$ (Bu$^\beta$) ester. Distillation of Pr γ-hydr-oxy-*n*-valerate under atm. pressure gives *n*-valero-lactone and PrOH, and a similar decomp. occurs when the Me and Et esters are distilled repeatedly at 2·5 mm. A little Et valerate is formed during the reduction of Et lævulate. H. BURTON.

Alkyl oxalates and oxamates. P. P. T. SAH and S. CHIEN (J. Amer. Chem. Soc., 1931, 53, 3901—3903). —Me, Et, Pr, b. p. 214—215°, Pr$^\beta$, b. p. 193—194°, Bu, b. p. 247—249°, and Bu$^\beta$, b. p. 229—231°, oxalates (convenient method of prep. given) are converted by aq. NH_3 (d 0·9; 1 mol.) in EtOH into Me, m. p.

122—123°, Et, m. p. 114—115°, Pr, m. p. 90—92°, Pr$^\beta$, m. p. 86—87°, Bu, m. p. 82—84°, and Bu$^\beta$, m. p. 75—76°, oxamates, respectively. H. BURTON.

Alkyl derivatives of ethyl malonate and ethyl cyanoacetate. G. R. CLEMO and C. R. S. TENNIS-WOOD (J.C.S., 1931, 2549—2551).—An improved prep. for β-chloroethyl toluene-*p*-sulphonate is described. Action of β-cyanoethyl toluene-*p*-sulphonate on Et sodiomalonate gives (a) *Et* β-*cyano-ethylmalonate*, b. p. 165°/18 mm., 135°/0·2 mm. (yield 63%), converted by HCl in EtOH into Et propane-αγγ-tricarboxylate; or (b) *Et di-(β-cyano-ethyl)malonate*, m. p. 61·5°, b. p. 200—205°/0·2 mm. (yield 80%), converted by HCl in EtOH into Et pentane-αγγε-tetracarboxylate, and by KOH in EtOH into pentane-αγγε-tetracarboxylic acid, m. p. 184° (decomp.) (cf. J.C.S., 1896, 69, 1509).
A. A. LEVI.

Properties of conjugated compounds. XII. Addition of esters to butadiene esters and ketones : effect of constitution on the αβ,αδ-ratio. E. H. FARMER and T. N. MEHTA (J.C.S., 1931, 1904—1913).—The ratio αβ/αδ-addition of esters to various butadiene derivatives in presence of traces of NaOR has been determined either (a) by catalytic reduction and separation of the dibasic acids formed, or (b) by separation of the products of ozonolysis. The figures in brackets give the % of αβ-addition in each case. The additive products of Me malonate and Me sorbate (A., 1930, 1163) are now found to yield tricarballylic acid on ozonolysis, corresponding with 9% of the αβ-product. Me malonate and Me Δ^{αγ}-*n*-pentadienyl ketone afford a mixture, b. p. 170—175°/18 mm., of *Me* β-*acetonyl*-Δ$^\gamma$-*pentene-αα-dicarboxylate* [29% as β-propylglutaric acid by (a); 27% as tricarballylic acid by (b)] and *Me* ε-*acetyl*,β-*methyl*-Δ$^\gamma$-*pentene-αα-dicarboxylate*. Addition of Et malonate to Et β-methylsorbate (improved prep.) affords a mixture, b. p. 170—175°/10 mm., of *Et* β-*methyl*-Δ$^\gamma$-*hexenoate*-β-*malonate* [>7% by (b)] and *Et* βδ-*dimethyl*-Δ$^\beta$-*pentene-αεε-tricarboxylate*, whilst Et cyanoacetate and Et γ-methylsorbate give a product, b. p. 190—195°/18 mm. [70% by (b); 74·5% by hydrolysis and subsequent ozonolysis].
J. W. BAKER.

Conjugated compounds. XIII. Michael re-action and manner of formation of saturated double-additive products. E. H. FARMER and T. N. MEHTA (J.C.S., 1931, 2561—2568).—The possible modes of formation of saturated additive compounds from butadienoid esters and, *e.g.*, Et malonate are discussed. Crotonaldehyde (1 mol.) and Et malonate (3 mols.) in presence of EtOH–NaOEt (1 mol.) give a product which after hydrolysis with 35% HCl and re-esterification affords *Et* 3-*methylcyclohexanone-5-acetate* (I), b. p. 140°/11 mm. (*semicarbazone*, m. p. 152°), and *Et* β-*methylpimelate*-β'-*acetate* (II), b. p. 187—188°/11 mm. (free *acid*, m. p. 130°). Dieckmann condensation of (II) gives *Et* 3-*methylcyclohexanone-6-carboxylate-5-acetate*, b. p. 170—172°/11 mm. (*phenylhydrazone*, m. p. 111°), hydrolysed (with loss of the 6-CO_2H group) to 3-*methylcyclohexanone-5-acetic acid*, b. p. 185°/9 mm., m. p. 77° (*Ag* salt; *semicarbazone*, m. p. 218°), and

oxidised by 3% $KMnO_4$ to oxalic and β-methyl-glutaric acids. H. Burton.

Thioketonic esters. I. Synthesis of ethyl thioacetoacetate and its derivatives. S. K. Mitra (J. Indian Chem. Soc., 1931, 8, 471—474).—Et β-chlorocrotonate (cis or trans form, or a mixture of both) with KSH, first at 0° and then under reflux, gives *Et thioacetoacetate* (I), orange, b. p. 75°/15 mm., which, since it decolorises I in EtOH, contains some of the enolic form, *Et β-thiolcrotonate*. With 10% H_2SO_4, KOH, or NaOH (I) yields $COMe_2$, H_2S, and CO_2. When boiled with 1 mol. of KOH in EtOH (I) gives a mixture of K thioacetoacetate and aceto-acetate together with K_2S. With Na in Et_2O, but not with NaOEt in EtOH, (I) gives the *Na* salt, a hygroscopic powder; with $NHPh·NH_2$, H_2S and a mixture of phenylmethylpyrazolone and the *substance* (II) are formed, the pro-portion of the latter increasing with the amount of $NHPh·NH_2$ used. p-Sulpho- and p-nitro-phenyl-methylpyrazolone were similarly prepared.
R. S. Cahn.

Mechanism of the Cannizzaro reaction with formaldehyde. H. S. Fry, J. J. Uber, and J. W. Price (Rec. trav. chim., 1931, 50, 1060—1065).—The view of Birstein and Labanov (A., 1927, 319) that the conversion of CH_2O into HCO_2Na and McOH by the Cannizzaro reaction is represented by consecutive reactions (a) $CH_2O+NaOH\longrightarrow HCO_2Na+H_2$ and (b) $CH_2O+H_2\longrightarrow MeOH$ has been confirmed stoicheio-metrically by addition to the reaction mixture of $CuSO_4$, the reduction of which to Cu competes with reaction (b). Determination of the free H_2 liberated (x), the H_2 equiv. (y) to the reduced Cu, and that (z) equiv. to the McOH formed proves that, within experimental error, the sum $x+y+z$=the total quantity of H_2 formed by reaction (a), as ascertained by determination of the amount of HCO_2Na produced. The same data show that 76—83% of the initial CH_2O reacted in conformity with equation (a) and the remainder in conformity with (b), the sum of these quantities being equal to the whole of the CH_2O used.
J. W. Baker.

Formaldehyde and its polymerides. F. Walker (Ind. Eng. Chem., 1931, 23, 1220—1222).—A review.

Constitution of artificial resins. I. Condensation products from thiocarbamide, form-aldehyde, and cuprous chloride. G. Walter and K. Oesterreich (Kolloidchem. Beih., 1931, 34, 115—162).—Yellow, viscous solutions with identical properties are obtained by interaction of $[CuThi_3]Cl$ $[Thi=CS(NH_2)_2]$ with CH_2O (6 mols.), or of equiv. amounts of CuCl, $CS(NH_2)_2$, and CH_2O, or of CuCl and mono- or s-di-(hydroxymethyl)thiocarbamide in H_2O. The presence of the CH_2 group (presumably in the combination $:N·CH_2·N:$) is proved by a Herzig–Meyer determination. Evaporation of the first yields a resin of the approx. composition $[CuThi_3]Cl,2CH_2O$, and flocculation with KCl of the second gives a ppt. of $[CuThi(H_2O)_2]Cl$, in marked contrast to the behaviour of an untreated solution of

$[CuThi_3]Cl$. The third method, using cold freshly-prepared solutions, gives a final ratio of $1Cu : 3CS(NH·CH_2·OH)_2$, and polymerisation, e.g., by heating, leads to a decrease of Cu in the ppt. formed with KCl. Identical ppts. are obtained from both mono- and di-hydroxymethyl derivatives after CuCl treatment. These relations are explained on the assumption that polymerisation occurs with the formation of cyclic structures (annexed formula) in addition to the normal chain polymerides, such structures being most probably linked through Cu into co-ordinated complexes with thiocarbamide. The identity of the products from mono- and di-(hydroxymethyl)thio-carbamides is readily explained only by the initial formation of dicyclic products, and this is supported by analysis of the ppts. if it is assumed that Cu can only be linked to sec.-N.

Cryoscopic measurements of aged solutions of di-(hydroxymethyl)thiocarbamide indicate decomp. into simpler mols. (unidentified), and similar measurements after CuCl treatment suggest that polymerisation under mild conditions leads merely to an increase in the no. of dicyclic polymerides. More complex resins (tetracyclic?) are produced with loss of CH_2O and H_2O by more prolonged heating. $HAuCl_4$, $HgCl_2$, and $Pb(NO_3)_2$ are without the action of Cu salts. Measurements of the conductivity of the various "resin" solutions and flocculation by various electrolytes of these and of $[CuThi_3]Cl$ are appended. In accordance with previous conductivity measure-ments, $[CuThi_3]Cl$ behaves as a colloid in H_2O.
H. A. Piggott.

Action of sulphuric acid on aldehyde cyano-hydrins. J. Verhulst (Bull. Soc. chim. Belg., 1931, 40, 475—496).—The compounds formed by the action of conc. H_2SO_4 on the cyanohydrins of $COMe_2$, COMeEt, $COEt_2$, and $COPr_2$ are acids of the type $CR_2(CO·NH_2)·OSO_3H$ [Na salts (all $+1H_2O$)] and not $OH·CR_2·C(:NH)·OSO_3H$ as previously described (this vol., 471). The cyanohydrins of CH_2O, MeCHO, EtCHO, PrCHO, $Pr^βCHO$, BuCHO, and $Bu^βCHO$ are similarly converted into the acids $CHR·(CO·NH_2)·OSO_3H$ [Na salts (all $+1H_2O$) (crystall-ographic data given in many cases)], which are hydrolysed much less readily both by 0·2N-HCl (with formation of H_2SO_4) and -NaOH (with production, in most cases, of mainly the salt $CO_2Na·CHR·OSO_3Na$) than those from the ketone cyanohydrins. Heptalde-hyde cyanohydrin is converted directly by H_2SO_4 into α-hydroxyoctoamide. H. Burton.

[Attempts to prepare] ketones and related products from paraffin hydrocarbons. J. F. Mesmer and R. A. Baxter (Colorado Sch. Mines Mag., 1931, 21, No. 6, 9—10).—In unsuccessful experiments CO_2 and CH_4 were passed over $ZnCO_3$ or $Zn(OAc)_2$ at 300° and 80 lb. pressure.
Chemical Abstracts.

Formation of unsaturated ketones from sub-stituted aminomethylene ketones. E. Benary (Ber., 1931, 64, [B], 2543—2545).—Addition of Me β-dimethylaminovinyl ketone in Et_2O to MgPhBr results mainly in the production of styryl Me ketone.

Similarly, Me β-dimethylamino-α-methylvinyl ketone and MgMeI or MgEtBr yield, respectively, Me α-methyl-Δ^α-propenyl ketone, b. p. 137°, and *Me α-methyl-Δ^α-butenyl ketone*, b. p. 55—60°/14 mm., obtained also from β-piperidino-α-methylvinyl Me ketone. β-Diethylaminovinyl Pr^α ketone and MgEtBr give *Pr^α Δ^α-butenyl ketone*, b. p. 68·72°/25 mm. Ph β-dimethylaminovinyl ketone is transformed by MgPhBr into PhOH, Ph$_2$, and Ph styryl ketone and by MgEtBr into *Ph Δ^α-butenyl ketone*, b. p. 250—252°/atm., 130—131°/22 mm. H. WREN.

Synthesis of n-propyl n-amyl ketone by Karrer and co-workers. S. A. BRYANT and G. R. CLEMO (J.C.S., 1931, 2080—2082).—Contrary to Karrer and others (A., 1929, 200) the ketone obtained by Bouveault and Locquin (A., 1905, i, 18) by hydrolysis of Et ethyl-n-hexoylacetate is Pr^α n-amyl ketone, the semicarbazone, m. p. 73—74°, of which is not depressed by that (also raised to m. p. 72° by repeated crystallisation) of the ketone prepared by Karrer's method (*loc. cit.*), but is depressed by the semicarbazone of Pr^β n-amyl ketone. Karrer's ketone is contaminated with Et n-hexoate, which is removed by treatment with KOH in MeOH. Recrystallisation of the semicarbazone, m. p. 65—66°, of the thus purified ketone (correct analysis) raises it to m. p. 73°, but this derivative now gives low C vals. on analysis. No such anomalies are observed with the p-*nitrophenylhydrazone*, m. p. 84—85°, which should be used in confirming the structure of the ketone obtained from lupinine. J. W. BAKER.

Ring structure of normal methylriboside. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1931, 93, 623—630).—Methylriboside (I) (this vol., 938) is methylated (Me$_2$SO$_4$ and NaOH in COMe$_2$ followed by MeI and Ag$_2$O) to *trimethylmethylriboside*, b. p. 54°/0·05 mm., [α]$_D^{24}$ −35·0° in H$_2$O, hydrolysed by dil. HCl to 2 : 3 : 4-*trimethylribose* (II), m. p. 85—86°, [α]$_D^{27}$ (in H$_2$O) −51·7 → −40·0°. Oxidation of (II) with Br–H$_2$O affords *trimethylribonolactone*, b. p. 93—95°/0·05 mm., [α]$_D^{27}$ +69·3° in CHCl$_3$, whilst oxidation with HNO$_3$ (d 1·42) and subsequent esterification gives Me i-trimethoxyglutarate. (I) and its derivatives are, therefore, of the pyranose type. H. BURTON.

" Active glucose "; concentration and reaction with mild oxidants. J. M. ORT (Proc. Staff Meetings Mayo Clinic, 1931, 6, 295—296).—When " active glucose " has been destroyed by an oxidant, more of the active reductant begins to form at once, immediately reduces the excess of oxidant, and then accumulates until the concentration reaches the equilibrium vals. After zero time when the last trace of oxidant has been reduced the reduction potential P at any time T, the equilibrium concentration X_E, the rate of formation of active glucose R, the equilibrium potential P′, and the potential at unit concentration of active glucose, P_0, are related by the expression $(P_0 − P)/(P_0 − P′) = 1 + [\log(e^{TR/X_E} − 1) − \log e^{TR/X_F}/ \log X_E]$. Approx. the same amount of active glucose (10^{-5} g.-equiv. per 60 g. of dextrose) is present at all p$_H$ vals. from 7 to 10. CHEMICAL ABSTRACTS.

Methylglucose of Pacsu. R. SCHINLE (Ber., 1931, 64, [B], 2361—2363).—The methylglucose,

m. p. 157° after slight softening at 150°, [α]$_D^{20}$ +23·5° to +65·3° in H$_2$O, obtained by Pacsu (A., 1925, i, 1242) (improved prep.) is shown by direct comparison and by the identity of its phenylhydrazone, m. p. 177°, and phenylosazone, m. p. 205° when rapidly heated, to be 2-methylglucose (cf. Brigl and Schinle, this vol., 71; Levene and others, *ibid.*, 825). H. WREN.

Syntheses of sugars. X. Preparation of 2 : 3 : 6-triacetyl-β-methyl-d-glucoside and its application to the synthesis of cellobiose derivatives. B. HELFERICH and H. BREDERECK (Ber., 1931, 64, [B], 2411—2414).—β-Methyl-d-glucoside 2 : 3 : 6-triacetate is isolated by treating the mixture of acetates obtained by partial acyl migration from the 2 : 3 : 4-compound with CPh$_3$Cl (cf. A., 1930, 1411) whereby the desired compound is unchanged and can be separated from the other products by virtue of its solubility in H$_2$O. It condenses with acetobromoglucose in presence of Ag$_2$CO$_3$, CaCl$_2$, I, and CHCl$_3$ to β-methylcellobioside hepta-acetate (identified by microscopic m. p. and mixed m. p.) Glucose 1 : 2 : 3 : 6-tetra-acetate and acetobromoglucose yield cellobiose octa-acetate, and 4-methylglucose is obtained by methylation of β-methylglucoside 2 : 3 : 6-triacetate. H. WREN.

Structure of glucal. E. L. HIRST and C. S. WOOLVIN (J.C.S., 1931, 1131—1137).—Triacetylglucal (I) behaves normally (cf. A., 1930, 1411) with BzO$_2$H giving a mixture of dextrose and mannose (after deacetylation), isolated as osazone and phenylhydrazone, respectively. Simultaneous deacetylation and methylation of (I) with Me$_2$SO$_4$, and 30% NaOH in COMe$_2$ at 47°, followed by MeI and Ag$_2$O, gives *trimethylglucal*, b. p. 45°/0·03 mm., [α]$_D^{18}$ +19·6° in H$_2$O (probably contaminated with a ψ-glucal derivative). This is oxidised by BzO$_2$H in H$_2$O to a trimethylglucose (further methylated to 2 : 3 : 4 : 6-tetramethylglucopyranose), and is converted by 2N-H$_2$SO$_4$ into 3 : 4 : 6-trimethyl-2-deoxyglucose (II) (this vol., 71). These reactions prove the presence of a pyranose ring in glucal (as I), and that no migration of Ac groups occurs in the prep. of I by reduction of acetobromoglucopyranose. Oxidation of (II) with Br in H$_2$O at 35—40° affords 3 : 4 : 6-trimethyl-2-deoxygluconic acid (*phenylhydrazide*, m. p. 125°) as its lactone, the rate of hydrolysis of which in H$_2$O at 19° is the same as that of tetramethyl-δ-mannonolactone (30% of lactone at equilibrium). J. W. BAKER.

CH$_2$·OAc

(I.)

Hydrogenation of kojic acid and its relationship to the products of dismutation of the sugars. K. MAURER (Ber., 1931, 64, [B], 2358—2360).—Hydroxyglucal tetra-acetate is treated with Cl$_2$ in anhyd. Et$_2$O until the yellow colour persists, the solution is rapidly evaporated in vac., and the product, dissolved in Et$_2$O, is treated with NaHCO$_3$. Acetylation with Ac$_2$O and pyridine followed by hydrolysis with NH$_3$–EtOH affords kojic acid (5-hydroxy-2-hydroxymethyl-4-pyrone) in good yield. Tetrahydrogenation of kojic acid in presence of colloidal Pd, followed by the action of NHPh·NH$_2$, leads to a
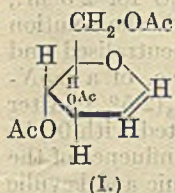
phenylosazone $C_{18}H_{22}O_2N_4$, m. p. 169°, which is the racemic form of the phenylosazone derived by Bergmann and Zervas (this vol., 939) from hydroxyglucal tetra-acetate. H. WREN.
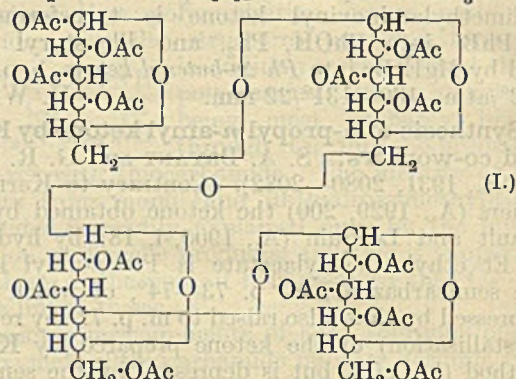
Effect of a 2-p-toluenesulphonyl group on the reactivity of the halogen atom of a glucosidyl halide. T. M. REYNOLDS (J.C.S., 1931, 2626—2630).—3 : 4 : 6-Triacetyl-β-glucosidyl chloride and *p*-Me·C₆H₄·SO₂Cl in presence of pyridine and CHCl₃ give 2-p-*toluenesulphonyl*-3 : 4 : 6-*triacetyl-α-glucosidyl chloride* (I), m. p. 121—122°, $[\alpha]_D^{16\cdot5}$ +134·8° in CHCl₃, the Cl atom of which is comparatively inactive. (I) is unaffected by Ag₂O or Ag₂CO₃ in cold MeOH, does not react with MeOH at 20—24°, but is converted by AgNO₃ and pyridine in boiling MeOH into 2-p-*toluenesulphonyl*-3 : 4 : 6-*triacetyl-β-methylglucoside*, m. p. 157—157·5°, $[\alpha]_D^{24}$ +3·4° in CHCl₃. α- and β-Glucosidyl halides when dissolved in pyridine show similar changes in rotation as in MeOH (cf. A., 1928, 873; 1929, 1167). H. BURTON.

Iodometric determination of lævulose. J. FIEHE and W. KORDATZKI (Z. Unters. Lebensm., 1931, 62, 516—522).—Auerbach and Bodländer's method (A., 1924, ii, 127) may be used for the determination, by difference, of dextrose+lævulose if the iodometric determination is applied before and after destruction of the lævulose by heating 25 c.c. of 1% solution with 10 c.c. of 5N-HCl in boiling H₂O for 2·5 hr., 27 c.c. of 5N-NaOH then being added, the solution diluted to 100 c.c., and 20—40 c.c. neutralised and mixed with 50 c.c. of N-I and 133 c.c. of a 0·5N-mixture of NaHCO₃ (97·5%) and Na₂CO₃ (2·5%). After 2 hr. in the dark the residual I is titrated with 0·1N-Na₂S₂O₃. Under these conditions the influence of the decomp. products of the lævulose (humic and lævulic acids, HCO₂H, etc.) is minimised. In presence of 0·1N-NaOH the amount of I consumed may be high by >1 c.c. J. GRANT.

Action of perbenzoic acid on substituted glucals. II. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1931, 93, 631—644).—Bromotetra-acetylgalactose, Zn dust, and 50% AcOH at 0° give *triacetylgalactal* (I), b. p. 134°/0·01 mm., m. p. 30°, $[\alpha]_D^{23}$ −12·4° in CHCl₃, converted by BzO₂H in CHCl₃ into 1-*benzoyl*-3 : 4 : 6-*triacetylgalactose*, m. p. 189°, $[\alpha]_D^{20}$ +24·0° in CHCl₃. This is acetylated by Ac₂O in pyridine at 0° to 1-*benzoyl*-2 : 3 : 4 : 6-*tetra-acetyl-galactose*, m. p. 122°, $[\alpha]_D^{23}$ −2·98° in CHCl₃, also prepared (with $[\alpha]_D^{23}$ +0·15° in CHCl₃) from AgOBz and bromotetra-acetylgalactose. Hydrolysis of (I) with Ba(OH)₂ in H₂O, or, better, with Ba(OMe)₂ in MeOH, gives *galactal (talal)*, m. p. 100°, which with BzO₂H in H₂O–EtOAc gives mainly talose and a little galactose (p-*bromophenylhydrazone*, m. p. 168—169°). The C₃–OH group in "glucals" appears to have a directive influence since the major product always contains C₂– and C₃–OH groups *cis* to one another; with C₃–OMe or –OAc, *trans* addition of C₂–OH occurs. Various methods of prep. and interconversion of some of the rarer sugars (*e.g.*, gulose, idose, altrose) are predicted. H. BURTON.

Action of mercury salts on acetohalogeno-sugars. VIII. Synthesis of 1-β-methyl-6'-β-cellobiosidogentiobiose trideca-acetate. G. ZEMPLÉN and A. GERECS (Ber., 1931, 64, [*B*], 2458—2461; cf. this vol., 716).—6-β-Cellobiosidoglucose acetate is converted by a 50% excess of 1-β-methylglucose triacetate in presence of Hg(OAc)₂ and boiling C₆H₆ into 1-β-*methyl-6'-cellobiosidogentiobiose trideca-acetate* (1), m. p. 236—237°, $[\alpha]_D^{19}$ −16·35° in CHCl₃.

Hydrolysis with NaOMe yields a colourless, non-cryst. *powder*, m. p. 100—110° after softening at 70°, $[\alpha]_D^{21}$ −30·34° in H₂O. If only a 10% excess of the glucoside is employed, 1-β-*methyl-6'-α-cellobiosidogentiobiose trideca-acetate* is produced in considerable quantity, but it could not be isolated. H. WREN.

Behaviour of stachyose when heated in glycerol. S. MURAKAMI (Acta Phytochim., 1931, 5, 267—270). Stachyose remains unchanged after heating for 2 hr. at 90—95° or 6 hr. at 140°. F. R. SHAW.

Constitution of myricitrin. S. HATTORI and K. HAYASHI (Acta Phytochim., 1931, 5, 213—218).—Methylation of myricitrin with diazomethane and hydrolysis with 2% H₂SO₄ affords myricetin 5 : 7 : 3′ : 4′ : 5′-pentamethyl ether (I); the conclusion is reached that the rhamnose residue in the glucoside is in the 3-position [Perkin (J.C.S., 1902, 81, 208) gives the 4′-position)]. Similarly, methylation with Me₂SO₄ and alkali in an atm. of H₂ results in a *Me₆* derivative, hydrolysed to (I). F. R. SHAW.

Glucosides. IV. Aesculin. A. K. MACBETH (J.C.S., 1931, 1288—1290).—Aesculin is converted either by KOH and MeI in MeOH or by diazomethane in Et₂O into 7-O-methylaesculin, hydrolysed by 2% H₂SO₄ to methylaesculetin. Repeated and prolonged methylation of methylaesculin with MeI and Ag₂O affords pentamethylaesculin, which could not be crystallised, but is hydrolysed by 1% HCl in MeOH to tetramethylglucopyranose. In support of Head and Robertson's conclusions (this vol., 73), aesculin is 6-β-glucosidoxy-7-hydroxycoumarin, the sugar being a pyranose form. J. W. BAKER.

Synthesis of glucosides. VIII. Synthesis of monotropitoside (gaultherin). A. ROBERTSON and R. B. WATERS (J.C.S., 1931, 1881—1888).—Me salicylate condenses with O-tetra-acetyl-α-glucosidyl bromide in the presence of Ag₂O and quinoline to form its O-tetra-acetyl-β-glucoside, m. p. 158—160°, $[\alpha]_{5461}^{21}$ −48·35° in COMe₂, hydrolysed by NH₃ in MeOH at 0° to the β-glucoside, m. p. 196—197°, $[\alpha]_{5461}^{21}$ −68·83° in H₂O (probably identical with the compound, m. p. 105°, of Karrer and Weidmann, A.,

1920, i, 395). This with CPh_3Cl in dry pyridine gives the 6-*triphenylmethyl ether*, m. p. 149°, $[\alpha]_{5461}^{20}$ $-5\cdot14°$ in $COMe_2$, the 2:3:4-Ac_3 derivative, m. p. 125°, $[\alpha]_{5461}^{20}$ $-34\cdot84°$ in $COMe_2$, of which is hydrolysed by HBr in AcOH to the 2:3:4-*O-triacetyl-β-glucoside* of Me salicylate, m. p. 152—153°, $[\alpha]_{5461}^{20}$ $-50\cdot87°$ in Me_2CO. This condenses with *O*-triacetylxylosidyl bromide in the presence of Ag_2O in C_6H_6 at 33—35° (poor yield in $CHCl_3$) to *monotropitoside hexa-acetate*

$$o\text{-}CO_2Me\cdot C_6H_4\cdot O\cdot CH{<}^{[CH\cdot OAc]_3}_{\quad O}{>}CH\cdot$$

$$CH_2\cdot O\cdot CH{<}^{[CH\cdot OAc]_3}_{\quad O}{>}CH_2,\ \text{m. p. } 189°,\ [\alpha]_{5461}^{20}$$

$-85\cdot8°$ in $CHCl_3$, identical with a specimen prepared by acetylation of the natural glucoside from *Gaultheria procumbens* (A., 1925, i, 347), and converted into a specimen identical with the latter on deacetylation with NH_3 in MeOH. Hence in primeverose the xylose and dextrose units are both pyranose and the glucosidic linkings are of the β-type. By similar methods the β-*xyloside* $+0\cdot5H_2O$ and anhyd., m. p. 173°, $[\alpha]_{5461}^{21}$ $-46\cdot01°$ in H_2O (Ac_3 derivative, m. p. 109—110°, $[\alpha]_{5461}^{21}$ $-62\cdot3°$ in $COMe_2$) and *rhamnoside* $+3H_2O$ and anhyd., m. p. 233° (decomp.), $[\alpha]_{5461}^{21}$ $+22\cdot64°$ in H_2O (Ac_3 derivative, m. p. 109°, $[\alpha]_{5461}^{21}$ $-11\cdot36°$ in $COMe_2$), of Me salicylate are also prepared. The former is partly hydrolysed by emulsin in H_2O at 37°, but the latter is unattacked.   J. W. BAKER.

Behaviour of zinc chloride in the esterification of cellulose. W. FREY and E. ELÖD (Ber., 1931, 64, [B], 2556—2561).—The following evidence is adduced in favour of the view that the enhanced rate of formylation of cellulose in simultaneous presence of $ZnCl_2$ and HCl as compared with the sum of the rates in the presence of each catalyst singly is due to the formation of complexes of the type $[ZnCl_2,Cl]H$ or $[ZnCl_2\cdot O\cdot CO\cdot H]H$. HCO_2H containing $ZnCl_2$ can dissolve much greater amounts of HCl than in absence of the salt. The electrical conductivity of HCO_2H containing $ZnCl_2$ and HCl is much greater than the sum of the corresponding conductivities of the acid containing $ZnCl_2$ and HCl singly. Transport measurements show that Zn wanders to the anode. The strongly acidic nature of the complex is established by the coloration given by its solution to safranine compared with those imparted by HCl and H_2SO_4 of known concentration. Parallelism exists between the strength of the acids and the rate of dissolution of cellulose.   H. WREN.

Synthetic cellulose and textile fibres from dextrose. H. HIBBERT and J. BARSHA (J. Amer. Chem. Soc., 1931, 53, 3907).—The membrane formed by the action of *Acetobacter xylinum* on dextrose is a true cellulose, since various derivatives obtained from it are identical with those prepared similarly from cotton cellulose. The membranes formed similarly from lævulose, sucrose, mannitol, glycerol, and glyceraldehyde are probably all identical with cellulose.   H. BURTON.

Methylene ethers of carbohydrates. I. Cellulose methylene ether. F. C. WOOD (J.S.C.I., 1931, 50, 411—418T).—Acid condensing agents cannot lead to a complete conversion of cellulose (or other insoluble carbohydrate) into its methylene ether by

CH_2O, since it is unstable to acid and it is impossible to separate the unconverted portion. In presence of acid and controlled amounts of H_2O the product is absorbent or not to cuprammonium hydroxide or direct dyes according to whether the reaction is conducted in presence of large or small amounts of H_2O. This explains the discrepancy between Eschalier's and Bruckhaus' work. In Eschalier's original process, the two types of product have also been observed by the author. The hydroxymethyl structure for the products obtained by the action of H_2SO_4–CH_2O mixtures on cellulose is erroneous. Experiments are described on the methylenation of cellulose under alkaline conditions by a variety of agents. Under optimum conditions, *cellulose monomethylene ether*, $C_6H_7O_2(OH)(O_2CH_2)$, has been prepared by utilising Haworth's technique employed in the methylation of sugars. This ether has a fibrous structure, is stable to alkali, but unstable to mineral acid, thus resembling the *iso*propylidene sugars. It is probably a 2:3-monomethylene cellulose with the 6-OH group free. It may be methylated in the usual way without disturbing the methylene group, but the process is difficult. Monochlorodimethyl sulphate reacts with soda-cellulose, giving a mixed Me methylene ether, with the possible intermediate formation of chloromethylcellulose. Neither the *iso*propylidene derivative nor the true thiocarbonate could be obtained from soda-cellulose, CMe_2Cl_2, and $CSCl_2$, respectively.

Lichenin and lichenin nitrate. J. REILLY, (Miss) M. HAYES, and P. J. DRUMM (Proc. Roy. Irish Acad., 1931, 40, B, 102—105).—Lichenin purified through its acetate gives a *pentanitrate*, similar in properties to cellulose nitrate.   A. A. LEVI.

Pine-wood lignin. B. RASSOW and H. GABRIEL (Cellulosechem., 1931, 12, 290—295).—The lignin (termed "glycol-lignin") is isolated in 22% yield from the air-dried wood-meal (5 g.) by extraction with 100 c.c. of glycol (previously treated at 160° with 0·1 c.c. of 25% HCl) at 165—170° for 5 min., precipitation from the extract with H_2O, subsequent dissolution in AcOH and re-precipitation, and extraction with Et_2O; other modifications of the purification process are described. The OMe and Ac contents, composition, colour reactions, and solubility of the lignins are given; the analytical results vary with the method of purification.   H. BURTON.
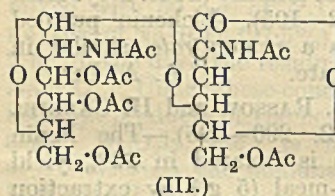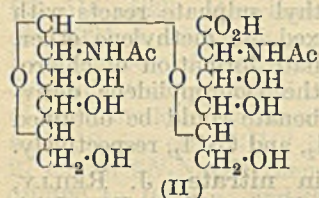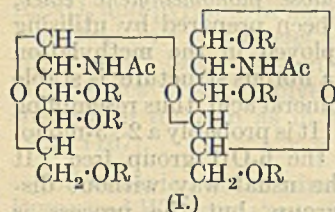
Formula of fir-wood lignin. P. KLASON (Svensk Kem. Tidskr., 1931, 43, 226—234).—By evaporation of the waste sulphite liquors almost to dryness at 80°, a brown residue is obtained sol. in H_2O with production of a non-dialysable solution. Addition of $C_{10}H_7\cdot NH_2$ to the solution gives a dark-coloured ppt. of a naphthylamine *salt*, $C_{38}H_{39}O_{13}NS$. The name *melaligninsulphonic acid* is proposed for the acid, which is regarded as a polymeride of β-ligninsulphonic acid, and *melalignin* for the corresponding lignin. The lignin present in wood is regarded as composed of 64·6% of α-lignin, $6C_{10}H_{12}O_4$, and 35·4% of β-lignin, $2C_9H_9O_4Ac,C_{10}H_{12}O_4$; it is shown from determinations of the quantities of CaO and SO_2 taking part in the sulphite process that the reactions involved are in harmony with the above formulæ.   H. F. HARWOOD.

Degradation of wood to cellulose and nitro-lignin. K. KÜRSCHNER (Cellulosechem., 1931, **12**, 281—286).—A lecture.　　　　　　H. BURTON.

[Reaction of] monobromoamine with organo-magnesium halides. G. H. COLEMAN and C. B. YAGER (Proc. Iowa Acad. Sci., 1930, **37**, 250).—The yields of primary amines are much smaller than with NH_2Cl.　　　　　　CHEMICAL ABSTRACTS.

Chitin and chitobiose. M. BERGMANN, L. ZERVAS, and E. SILBERKWEIT (Ber., 1931, **64**, [*B*], 2436—2440).—Chitin is converted by Ac_2O and conc. H_2SO_4 into *chitobiose octa-acetate* (I; R=Ac), m. p. 289° (corr., decomp.), $[\alpha]_D^{20} +50\cdot3°$ in AcOH, hydrolysed by boiling dil. HCl to *d*-glucosamine hydro-chloride. It is con-verted by $0\cdot2N$-KOH into *diacetylchitobiose* (I; R=H), m. p. above 185° (decomp.). When treated with NaOI in presence of sufficient alkali to hydrolyse the OAc groups, the octa-acetate affords *diacetyl-chitobionic acid* (II), converted by boiling Ac_2O into *hexa-acetyl-anhydrochitobionolact-one* (III), m. p. 215° (corr.). Since only one double linking is hereby developed, it follows from analogy with the behaviour of glucosamic acid (this vol., 1402) that the OH group in position 4 or 5 is sub-stituted by the second glucosamine residue, whilst the presence of the double linking in the 2 : 3-position is deduced from the enhanced instability of the compound towards dil. HCl (with which NH_4Cl is produced) and by its ozonolysis to acetoxamic acid.　　　　　　H. WREN.

Preparation of glycine. H. KRAUSE (Chem.-Ztg., 1931, **55**, 666).—A solution of 378 g. of $CH_2Cl\cdot CO_2H$ in 1200 g. of H_2O ($\gg40°$) is mixed with the theoretical wt. of Cu in the form of a paste of oxide and carbonate. After 2 days the blue solution is filtered, made up to 2000 g. with H_2O, and mixed with 2 litres of 9% aq. NH_3 ($\frac{1}{4}$ in excess of theory). After 24 hr. at room temp. the liquid is boiled for 3 hr. under reflux and finally conc. to 1200 g. The separation of Cu aminoacetate is facilitated by adding 1500 c.c. of 75% EtOH and, after washing and drying, the Cu compound (350—360 g.) is converted into glycine by the action of H_2S. H. J. DOWDEN.

Preparation of sarcosine. W. COCKER and A. LAPWORTH (J.C.S., 1931, 1894—1898).—Glycine, either pure or by hydrolysis of aminoacetonitrile H sulphate with 40% H_2SO_4 at 125° (cf. this vol., 943), is converted (93 and 88% yield, respectively) b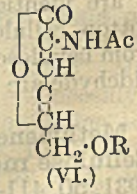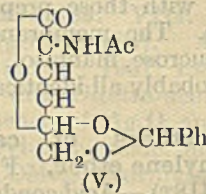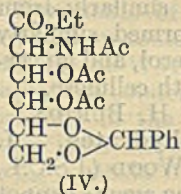y cold N-NaOH and $PhSO_2Cl$ into its N-benzenesulphonyl derivative, readily methylated (95% yield) with $3N$-NaOH and Me_2SO_4 to N-benzenesulphonylsarcosine. After hydrolysis of this with 40% H_2SO_4 at 125—130° the $PhSO_3H$ is readily removed as its Zn salt by addition of a saturated solution of $ZnSO_4$, the excess of which is removed by $BaCO_3$. Traces of Ba in the filtrate are removed by the requisite amount of dil. H_2SO_4 and evaporation affords crude cryst. sarcosine in 74% yield. The prep. of cryst. N-benzoylsarcosine in 50% yield by the action of BzCl and $NaHCO_3$ is described.　　　　　　J. W. BAKER.

Glucosamic acid and its deamination. M. BERGMANN, L. ZERVAS, and E. SILBERKWEIT (Ber., 1931, **64**, [*B*], 2428—2436).—Glucosamic acid is con-verted by Ac_2O and anhyd. NaOAc into the lactone (I), m. p. 154° (corr.), which reduces Fehling's and ammoniacal Ag solutions, is optically inactive, and is transformed by catalytic hydrogenation and sub-sequent hydrolysis into the stereoisomeric *α-amino-δε-dihydroxy-n-hexolactone hydrochlorides*, m. p. 165° (corr.) and 173—175° (corr.), respectively. Partial hydrogenation yields the *lactone* (II), m. p. 113° (corr.), in which the double linking is in the 2 : 3-position, since it is hydrolysed by dil. HCl to NH_4Cl and α-keto-δε-dihydroxy-*n*-hexolactone [*phenyl-hydrazone*, m. p. 179° (corr.)] and converted by ozonisation into the *compound* (?) $NHAc\cdot CO\cdot CO\cdot O\cdot CH(CH_2\cdot OH)\cdot CH_2\cdot CO_2H$, m. p. 131° (corr., decomp.), hydrolysed to acetoxamic acid [*phenylhydrazide*, decomp. 184° (corr.)]. The 4 : 5-position of the second double linking in (I) follows from the absence of an asymmetric C atom and the ready formation by means of conc. HCl of the *chlorohydrin* (III), m. p. 197°, which absorbs 2 mols. of H_2 and is easily converted by AgOAc into the original lactone. Further confirmation of the δ-lactonic structure is found in the transformation of the lactone by conc. AcOH and $NHPh\cdot NH_2$ into the *compound* $NHPh\cdot NH\cdot CO\cdot C(:N\cdot NHPh)\cdot CH_2\cdot CH_2\cdot C(:N\cdot NHPh)\cdot CH:N\cdot NHPh$, m. p. 219 (corr., decomp.). [A *substance*, (?) $NHPh\cdot NH\cdot CO\cdot C(:N\cdot NHPh)\cdot CH_2\cdot CH_2\cdot C(:N\cdot NHPh)\cdot CH_2\cdot OH$, m. p. 193° (corr.), is also obtained.] The possible deamination of glucosamic acid to αδ-diketo-ε-hydroxy-*n*-hexoic acid is thus established. Elimin-ation of H_2O in the 4 : 5-position during the acetyl-ation of glucosamic acid is not observed when the 5-OH is substituted. Thus Et 5 : 6-benzylidene-glucosamate hydrochloride, Ac_2O, and anhyd. NaOAc afford the Ac_3 derivative (IV), m. p. 119° (corr.), and
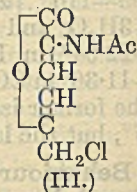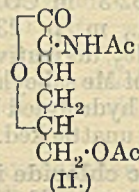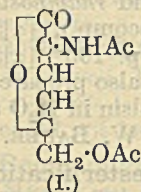
the singly unsaturated *lactone* (V), m. p. 198° (corr.), $[\alpha]_D^{20}$ −30·1° in $CHCl_3$. Removal of the benzylidene group from (V) by cold HCl is immediately followed by loss of H_2O, disappearance of optical activity, and production of the *lactone* (VI; R=H), m. p. 158·5° (corr.), which yields an Ac derivative (VI; R=Ac), m. p. 115° (corr.), from which a chlorohydrin is not obtained by the action of conc. HCl. H. WREN.

Cobalt complexes of cysteine. M. P. SCHUBERT (J. Amer. Chem. Soc., 1931, **53**, 3851—3861).— Cysteine hydrochloride and $CoCl_2$ in presence of aq. KOH and N_2 give at p_H 11—12, *K cobaltobiscysteinate* (I), $Co(RSK)_2,2H_2O$ [in this and other formulæ R= $\cdot CH_2 \cdot CH(NH_2) \cdot CO_2 \cdot$], whilst at p_H 7—8 *Co˙˙ cobaltobiscysteinate* (+2 and $4H_2O$) results. At p_H 5—6 in presence of O_2 the above reactants give the *complex* $Co(RSH)_3$ (+3 and $4H_2O$) [K_3 salt (II)], but at p_H 8—9 the K salt (+$4H_2O$) (III) of the *complex* $[Co(RSH)_2OH]_2,8H_2O$ [*Ba* salt (+$9H_2O$); unstable *trihydrochloride* (+H_2O); *picrate* (+$9H_2O$)] is formed. (I) is oxidised by H_2O_2 to an unidentified yellow complex. The ultra-violet absorption spectrum of (III) resembles that of K cobaltibisthiolacetate (this vol., 67), but that of (II) differs from that of cobaltitrisalanine. Co-ordination structures are suggested for (I), (II), and (III). H. BURTON.

Synthesis of carbamide from ammonium carbamate. B. NEUMANN.—See this vol., 1374.

Esterification of erythritol. J. SCHALIT (Wiss. Mitt. Oesterr. Heilmittelstelle, 1929, 42—44; 1930, 5—10; Chem. Zentr., 1931, i, 2602—2603).—Treatment of erythritol or its dichlorohydrin with palmitic or stearic acid leads to mixtures of esters. The quantities of the various esters obtained under different conditions are recorded. A. A. ELDRIDGE.

Reaction of chloropicrin with potassium iodide. G. D. SUICHER (J. Chem. Ind., Russia, 1930, **7**, 1168—1169).—The reaction $CCl_3 \cdot NO_2 + 4KI = CI_4 + 3KCl + KNO_2$ takes place with or without solvents; with less KI I-substituted derivatives of $CCl_3 \cdot NO_2$ are not obtained. Interaction between $CCl_3 \cdot NO_2$ and KBr is slow; CBr_4, $CBr_3 \cdot NO_2$, $CClBr_2 \cdot NO_2$, and other Br-substitution products are formed. CHEMICAL ABSTRACTS.

Formation and transformation of cyclic acid imides. W. HÜCKEL and H. MÜLLER.—See this vol., 1291.

Constitutional studies in the monocarboxylic acids derived from sugars. V. Hexonic and pentonic acid amides. Action of sodium hypochlorite on the isomeric trimethylarabonamides. R. W. HUMPHREYS, J. PRYDE, and E. T. WATERS (J.C.S., 1931, 1298—1304).—By the action of dry NH_3 in EtOH on the appropriate lactone (obtained by the action of Br and HBr in H_2O on the glucoside) the following pyranoid and furanoid amides have been obtained : 2 : 3 : 4 : 6-, m. p. 68°, $[\alpha]_D$ +60·4° in $COMe_2$ (previously described as the 2 : 3 : 5 : 6-compound, J.C.S., 1924, **125**, 1045), and 2 : 3 : 5 : 6-, m. p. 91°, $[\alpha]_D^{20}$ +39·2° in H_2O, -*tetramethylgluconamide*; 2 : 3 : 4 : 6-, m. p. 120°, $[\alpha]_D$ +37·9° in $COMe_2$ (A., 1925, i, 356), and 2 : 3 : 5 : 6-, m. p. 153° (slight decomp.), $[\alpha]_D$ +5·76° in $COMe_2$, -*tetramethylgalactonamide*; 2 : 3 : 4-,

m. p. 96°, $[\alpha]_D$ +35·5° in EtOH, and 2 : 3 : 5-, m. p. 132°, $[\alpha]_D$ +19·3° in EtOH, -*trimethylarabonamide*. 2 : 3 : 4-Trimethylarabonamide is converted by alkaline NaOCl into the internal *urethane*,

$$NH \begin{smallmatrix} [CH \cdot OMe]_3 \\ CO \end{smallmatrix}{-}\begin{smallmatrix} \\ O \end{smallmatrix}{>}CH_2 \ (I),$$

m. p. 142°, $[\alpha]_D$ +42° in H_2O, the 2 : 3 : 5-compound similarly yielding 2-*keto-4 : 5 : ω - trimethoxy - 6 - methyltetrahydro - 1 : 3 - oxazine*,

$$NH \begin{smallmatrix} [CH \cdot OMe]_2 \\ CO \end{smallmatrix}{-}\begin{smallmatrix} \\ O \end{smallmatrix}{>}CH \cdot CH_2 \cdot OMe \ (II),$$

m. p. 76°, $[\alpha]_D$ +5·0° in H_2O, converted by 1% HCl in MeOH at room temp. into an isomeric *compound* (III), m. p. 63—65°, $[\alpha]_D$ −178° in H_2O, similar treatment in a sealed tube at 80° giving a substance, m. p. 45—47°, which is probably a mixture of (II) and (III). Considerable change in rotation occurs when either (II) or (III) is treated with 1% NaOH in H_2O, (III) giving a *substance*, $[\alpha]_D$ −41°, possibly a dimethyltetrose.
J. W. BAKER.

Guanidine and nitrous acid. II. W. D. BANCROFT and S. L. RIDGWAY (J. Physical Chem., 1931, **35**, 2950—2963; cf. this vol., 1280).—Guanidine and HNO_2 do not react, but in the presence of HCl or H_2SO_4 the reaction is slow up to a certain concentration, sp. for each acid. At higher concentrations they react slowly, liberating 2 atoms of N; the third atom is evolved more slowly. The influence of various factors affecting the reaction and preliminary experiments on the decomp. products are discussed. Various formulæ for guanidine are also considered.
L. S. THEOBALD.

Ethylenic nitriles. α-Ethylcrotononitriles. P. BRUYLANTS and L. ERNOULD (Bull. Acad. roy. Belg., 1931, [v], **17**, 1027—1040).—Quinoline at 140—145° converts β-chloro-α-ethylbutyronitrile into a mixture of approx. 40% of the form (I), b. p. 139—140°/758 mm., and 60% of the form (II), b. p. 155—156°/760 mm. (A., 1927, 652), of α-ethylcrotononitrile which are interconvertible by heating with NaOPh. They are converted by H_2SO_4 into the corresponding stereoisomeric amides, m. p. 93—94° and m. p. 118—119° (*loc. cit.*, m. p. 109°). Irradiation of the amide, m. p. 118—119°, causes some conversion into the other form (together with other changes), whilst the amide of lower m. p. undergoes no appreciable change. Hydrolysis of the nitrile (II) affords only α-ethylcrotonic acid (*trans*), m. p. 41—42°, whilst under certain conditions of (incomplete) hydrolysis (I) affords a mixture of this acid and α-ethyl*iso*crotonic acid (*cis*), m. p. −22·5° to −21·8°, separated by means of their Ca salts (A., 1904, 906). J. W. BAKER.

Ethylenic nitriles. β-Ethylcrotononitrile. P. BRUYLANTS (Bull. Acad. roy. Belg., 1931, [v], **17**, 1008—1026).—β - Hydroxy - β - chloromethyl - *n*-butane is converted by KCN in EtOH into β-*hydroxy-β-ethyl-n-butyronitrile* (I), b. p. 106—107°/14 mm., dehydrated by H_2SO_4 to a mixture of αβ- and βγ-unsaturated nitriles (some COMeEt is also formed) from which only one *form* (II), b. p. 162—162·5°/752 mm., of β-methyl-Δα-pentenonitrile is obtained when the βγ-nitrile is removed as its dibromide. HCl converts (I) into the corresponding β-*chloronitrile*, b. p. 77—78°/11 mm. (together with some unsaturated nitrile containing 81% of the βγ-form), which with

quinoline at 130° again gives only the form (II), together with less of the βγ-nitrile than is obtained in the H₂SO₄ dehydration (A., 1929, 1294). Oxidation of β-methyl-*n*-butyl alcohol (from trioxymethylene and *sec.*-BuBr) to the aldehyde is best effected by air and a divided Ag catalyst at 330° (A., 1921, i, 218), the *cyanohydrin*, b. p. 115—115·5°/12 mm., of which is dehydrated by P₂O₅ into a mixture of unsaturated nitriles from which, after removal of the βγ-form by Br, a second stereoisomeric *form*, (III), b. p. 142—143°/765 mm., of β-methyl-Δ^α-pentenonitrile, together with (II) are isolated by fractional distillation. The two forms have also different vals. of *d* and *n* and differ in odour, and each is converted by cold conc. H₂SO₄ into the corresponding *amide*, m. p. 98—99° [*loc. cit.* from (II)] and m. p. 116—116·8° [from (III)]. Interconversion of these amides could not be effected by irradiation. J. W. BAKER.

Action of the Grignard reagent on amino-nitriles. T. S. STEVENS, J. M. COWAN, and J. MACKINNON (J.C.S., 1931, 2568—2572).—The following reactions occur between α-*tert.*-aminonitriles and Grignard reagents : NR‴R⁗·CR′R″·CO·R⁗‴ (I) ⟵ NR‴R⁗·CR′R″·CN+MgR⁗‴X ⟶ MgXCN +NR‴R⁗·CR′R″R⁗‴ (II) (cf. Bruylants, A., 1924, i, 984). (I) is produced [sometimes admixed with (II)] only when R′=R″=H. Thus, NMe₂·CH₂·CN and MgMeI give NMe₂Et and NMe₂·CH₂Ac ; with MgPhBr, NMe₂·CH₂Bz results. NEtPh·CH₂·CN and MgMeI afford *N*-ethylanilinoacetone, b. p. 143°/11 mm. (*phenylhydrazone*, m. p. 96°), also formed from NHEtPh and CH₂AcBr at 30° ; α-piperidinopropionitrile and MgPhBr yield 1-α-phenylethylpiperidine (*picrate*, m. p. 140—142°) ; α-dimethylaminophenylacetonitrile with MgMeI, MgPhBr, and CH₂Ph·MgCl furnishes α-phenylethyldimethylamine, benzhydryldimethylamine, and αβ-diphenylethyldimethylamine [*picrate*, m. p. 156—157° (softens at 130°) ; *hydrochloride*, m. p. 187—188°, converted by dry distillation into stilbene], respectively ; α-dimethylamino-β-phenylpropionitrile [*hydrochloride*, m. p. about 170° (decomp.)] and MgPhBr give αβ-diphenylethylamine. Reaction (II) is correlated with the ψ-basic properties of the corresponding *tert.*-amino-alcohols. In accordance with this view, 1-cyanohydrastinine and 9-cyano-9 : 10-dimethyl-9 : 10-dihydroacridine are converted by MgMeI into 1-methylhydrastinine and 9 : 9 : 10-*trimethyl*-9 : 10-*dihydroacridine* (also obtained from MgMeI and methylacridine methiodide), respectively. H. BURTON.

***tert.*-Phosphines containing higher alkyl radicals.** I. K. JACKSON, W. C. DAVIES, and W. J. JONES (J.C.S., 1931, 2109—2112).—By the action of the appropriate Grignard compound on PCl₃ or PPhCl₂ in absence of air the following phosphines are prepared : *tri*-n-*hexyl*-, m. p. about .20°, b. p. 227°/50 mm. (*oxide*) ; *phenyldi*-n-*hexyl*-, b. p. 236°/50 mm. [*oxide* ; *chloromercurate*, m. p. 140° ; *methiodide*, m. p. 67° (*chloroplatinate*, m. p. 135°)] ; *tri*-n-*heptyl* , m. p. about 20°, b. p. 260°/50 mm. (*oxide*) ; *phenyldi*-n-*heptyl*-, b. p. 260°/50 mm. [*chloromercurate*, m. p. 102° ; *methiodide*, m. p. 87° (*chloroplatinate*, m. p. 105°)] ; *tri*-n-*octyl*-, m. p. about 30°, b. p. 291°/50 mm. ; *phenyldi*-n-*octyl*-, b. p. 277°/50 mm. [*oxide* ; *methiodide*, m. p. 81° (*chloroplatinate*,

m. p. 102°)], -*phosphine*. The physical properties of the trialkyl- and phenyldialkyl-phosphines are discussed, the b. p./50 mm. of the members of these two homologous series being represented (error +2°) by $t=32·014M^{0·48587}-273$ and $t=41·583M^{0·44512}-273$, respectively ($M=$mol. wt.). J. W. BAKER.

Arsinosulphides of the fatty and aromatic series. A. E. KRETOV and A. Y. BERLIN (J. Gen. Chem. Russ., 1931, 1, 411—418).—A series of arsinosulphides was prepared by the action of H₂S, KHS, or Na₂S on the corresponding chloroarsines. Arsinosulphides of the type RAsS are generally polymerised : those of the type S(AsR₂)₂ are monomerides. The following were obtained : β-*chlorovinyl*- ; β-*hydroxyethyl*-, m. p. 66—70° ; β-*acetoxyethyl*-, m. p. 69° ; p-*cyanophenyl*-, m. p. 152° ; β-*naphthyl*-, m. p. 154° ; p-*chlorophenyl*-, m. p. 135° ; p-*nitrophenyl*-, m. p. 210° ; m-*nitrophenyl*-, m. p. 98—101° ; p-*ethoxyphenyl*-, m. p. 127—129°, -*arsinosulphide* ; p-*phenylenediarsinodisulphide*, m. p. 275—276°. E. B. UVAROV.

Action of boron fluoride on organic compounds. H. BOWLUS and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1931, 53, 3835—3840).—The following *compounds* are obtained when BF₃ (1 mol.) is passed into the requisite substance (1 mol.) at 25° : AcOMe,BF₃, b. p. 110°/739 mm., m. p. 60° ; AcOEt,BF₃, b. p. 119°/739 mm., m. p. 26° ; HCO₂Et,BF₃, b. p. 102°/748 mm. ; AcOPr,BF₃, b. p. 126°/743 mm. ; EtCO₂Et,BF₃, b. p. 116°/747 mm. ; Ac₂O,BF₃, m. p. 194° ; NH₂Ac,BF₃ (decomp. on attempted distillation). BuOH and BF₃ give an oil which gradually decomposes to a mixture of aliphatic and aromatic hydrocarbons, whilst AcOH and EtCO₂H yield the compounds (AcOH)₂,BF₃, b. p. 140°/746 mm., and (EtCO₂H)₂,BF₃, b. p. 62—63°/17 mm., respectively (cf. A., 1927, 836). The compound MeCN,BF₃ has b. p. 101°/752 mm., m. p. 87° (cf. A., 1891, 1441). Most of the above compounds are completely dissociated in the vapour phase. Cryst. additive compounds are formed from pyridine and 2 mols. of BF₃ and from quinoline and piperidine with 1 mol. of BF₃. The compound from 1 mol. of an alcohol (ROH) and 1 mol. of BF₃ is probably a co-ordination compound which subsequently ionises to [RO ⟶ BF₃]⁻+H⁺. The mechanism of acetal formation (A., 1930, 745, 1160) from C₂H₂,BF₃, and ROH is probably : (*a*) C₂H₂+ 2H⁺+2[RO ⟶ BF₃]⁻ ⟶ CHMe(OR BF₃)₂ (I) ; (*b*) (I) ⟶ CHMe(OR)₂+BF₃. H. BURTON.

Co-ordination compounds of boron trifluoride with oxygenated carbon derivatives. G. T. MORGAN and R. TAYLOR (Chem. and Ind., 1931, 869).—BF₃ combines additively with the esters of aliphatic acids and the following have been obtained in the cryst. state : HCO₂Me,BF₃, m. p. 23·5°, b. p. 94°/772 mm. ; HCO₂Et,BF₃, m. p. 3°, b. p. 103°/772 mm. ; AcOMe,BF₃, m. p. 61·5°, b. p. 112°/772 mm. ; AcOEt,BF₃, m. p. 31°, b. p. 123°/772 mm. ; Ac₂O,BF₃, m. p. 190° (decomp.). E. S. HEDGES.

Decomposition of ortho-ethers of monosilane on heating under pressure, and the liberation of free silicon. III. B. N. DOLGOV and J. N. VOLNOV (J. Gen. Chem. Russ., 1931, 1, 330—339).—Tetra-alkyl-

oxymonosilanes yield disilane derivatives on heating at 280° with H_2 under pressure, whilst at >280° unsaturated hydrocarbons and SiO_2 are produced. Under analogous conditions tetralkyloxymonosilanes decompose only at >280° to yield the corresponding phenol and amorphous Si. The ethers are less stable than are the corresponding silanes. Tetra*cyclo*hexyl orthosilicate decomposes at >380° to yield SiO_2 and *cyclo*hexene. R. TRUSZKOWSKI.

Reactions of inorganic vanadium compounds with magnesium phenyl bromide. C. C. VERNON (J. Amer. Chem. Soc., 1931, **53**, 3831—3834).—Varying amounts of Ph_2 are formed when MgPhBr is treated with VCl_2, VCl_3, $VOCl_3$, V_2O_3, V_2O_4, or V_2O_5 in Et_2O (cf. A., 1928, 50). A small amount of a solid V-containing compound (hydrolysed by H_2O to Ph_2) was obtained in one experiment from MgPhBr and $VOCl_3$. V does not react with EtBr, EtI, $Pr^\beta I$, BuCl, PhBr, PhI, $PhSO_2Cl$, ethylene dibromide, or *p*-dibromobenzene in Et_2O, or with CH_2PhCl, AcCl, or Me_2SO_4 in absence of solvent. H. BURTON.

Aromatic sulphonyl fluorides. Method of preparation. W. DAVIES and J. H. DICK (J.C.S., 1931, 2104—2109).—Aromatic sulphonyl fluorides are readily prepared (in glass vessels) by refluxing the sulphonyl chloride with 50% excess of KF in H_2O (the presence of H_2O is essential: NaF and ZnF_2 may be used) and thus are prepared a number of known sulphonyl fluorides (A., 1927, 963) and : 2-*chloro-5-nitro-*p-*toluene-*, m. p. 84—85°; 1 : 3-dimethylbenzene-4 : 6-di- (*loc. cit.*, described as the 2 : 4-disulphonyl compound); *chlorobenzene-*2 : 4-*di-*, m. p. 88—89°; 1 : 3-*dichlorobenzene-*4 : 6-*di-*, m. p. 141—143°; 1 : 3 : 5-*trichlorobenzenedi-*, m. p. 109—110°; 1 : 3-*dimethoxy-*(?-*benzene*)-4 : 6-*di-*, m. p. 209—211°; *benzene-*1 : 3 : 5-*tri-*, m. p. 166—167°; *chlorobenzene-*2 : 3 : 6-*tri-*, m. p. 179—181°, -*sulphonyl fluoride*. These are all more stable to acid and neutral hydrolytic agents than are the corresponding chlorides, but are quantitatively hydrolysed to NaF and the sulphonate by NaOH and are thus a convenient source of definite ionisable F concentration. J. W. BAKER.

Influence of directing groups on nuclear reactivity in oriented aromatic substitutions. II. Nitration of toluene. C. K. INGOLD, A. LAPWORTH, E. ROTHSTEIN, and D. WARD (J.C.S., 1931, 1959—1982).—Accurate data for the proportions of isomerides (ratio of the magnitudes which individually relate to the effect of the substituent Me on the reactivity at different nuclear positions) and the speed of total substitution relative to that of C_6H_6 (reduced velocity, *i.e.*, sum of such magnitudes) have been determined for nitration of PhMe in $AcNO_3$ at 30° (in AcOH alone or in excess of Ac_2O as solvent) by refinement of methods previously employed (A., 1928, 164). Under these conditions the mean val. of the reduced velocity is 23, the mean proportions of *o-*, *m-*, and *p*-nitrotoluenes formed (by oxidation methods and by thermal analysis) are 58·4, 4·4, and 37·2%, respectively, whence the partial rate factors (*F*, previously designated coeff. of activation=the factor by which the introduction of the directing group increases the probability of substitution at that atom during a small element of time under the conditions

of comparison) for the *o-*, *m-*, and *p*-positions are 40, 3·0, and 51, respectively ($\Delta E = +2·21$, $+0·66$, and $+2·36$ kg.-cal., respectively; cf. below). Thus the inductive ($+I$) effect of the Me group activates all three positions in PhMe, the *o-* and *p-* to a much greater extent than the *m-*. Alteration of the nitrating medium to HNO_3 in $MeNO_2$ causes no change in either the reduced velocity (21) or in the *F* val. (37, 28, and 47, respectively). With $AcNO_3$ at 0°, a higher reduced velocity (27) and higher *F* val. (47, 3·0, 62) were obtained (*o* : *m* : *p*-isomerides=58·1 : 3·7 : 38·2). The significance of these results is discussed and it is tentatively suggested that *F* may vary with temp in such a way that $\Delta E = RT \log_e F$, the ΔE's being a measure of the internal activation by the substituent Me for the various nuclear positions in PhMe. J. W. BAKER.

Action of magnesium on dibromotoluene and dibromo-*m*-xylene. J. S. SALKIND, S. KIRILLOVA, and N. NIKIFOROVA (J. Gen. Chem. Russ., 1931, **1**, 193—198).—Mg and 3 : 4-dibromotoluene interact slowly and with difficulty; both Br atoms react, mainly forming org. Mg compounds and some tarry products. Tribromotoluene does not react. 4-Bromo-*m*-xylene gives dimethylbenzoic acid. 4 : 6-Dibromo-*m*-xylene reacts when the Mg is activated by I, forming 4-bromo-*m*-xylene and a Mg org. compound which gives 5-bromo-2 : 4-dimethylbenzoic acid on decomp. with H_2O. The presence of the second Me group in the C_6H_6 ring hinders the reaction, allowing only one Br atom to react. E. B. UVAROV.

Preparation of cinnamyl chloride and its Grignard reagent. H. GILMAN and S. A. HARRIS (Rec. trav. chim., 1931, **50**, 1052—1055).—For the prep. of the compound $MgCl\cdot CHPh\cdot CH:CH_2$ in good yield the necessary cinnamyl chloride is best obtained by the action of $SOCl_2$ and pyridine in $CHCl_3$ on the alcohol. A prep. having a val. 76·8% by acid titration gave 57% by the I method (A., 1926, 535) and hence the observation that one RMgX mol. reacts with the ethylenic linking in another to form a new Grignard reagent which does not react with I (A., 1929, 802) is not confirmed. An efficient method for the conversion of a Grignard reagent into the carboxylic acid is described. J. W. BAKER.

Tetraphenyl-*o*-xylylene. G. WITTIG and M. LEO (Ber., 1931, **64**, [*B*], 2395—2405).—Me *o*-phthalate is readily transformed by LiPh in Et_2O into tetraphenyl-*o*-xylylene glycol, m. p. 203·5° (cf. Schlenk and Brauns, A., 1915, i, 519) (*Li* derivative). The superiority of LiPh over MgPhBr is shown by the smooth conversion by the former of Me diphenate into 2 : 2'-di(hydroxybenzhydryl)diphenyl, m. p. 252—253° (cf. A., 1926, 610). Similarly Me 2 : 2'-dimethoxydiphenate and LiPh afford 2 : 2'-*di-methoxy-*6 : 6'-*di(hydroxybenzhydryl)diphenyl*, m. p. 278—280° (*Li₂* derivative), converted by boiling AcOH into the corresponding *anhydride*, $C_{40}H_{32}O_3$, m. p. 314—316°, whereas the glycol does not appear to be formed with MgPhBr. Phthalic anhydride and LiPh give resinous matter and triphenylcarbinol. Tetraphenyl-*o*-xylylene glycol cannot be converted into the corresponding Me_2 ether by MeOH containing HCl on account of its ready anhydrisation to tetra-

phenylphthalane; the crude Li derivative does not react with MeI at 100°, whilst at 160° or 200° tetraphenylphthalane is produced. Treatment of the glycol with K in dioxan yields the corresponding *K* derivative, readily transformed by MeI into *tetraphenyl-o-xylylene glycol Me ether*, m. p. 195—196°, converted by MeOH containing HCl into tetraphenylphthalane. Treatment of the ether with K gives the *compound* $CPh_2K \cdot C_6H_4 \cdot CPh_2 \cdot OK$, also obtained from tetraphenylphthalane and Na–K in dioxan and converted by EtOH into 2-benzhydrylhydroxybenzhydrylbenzene, m. p. 216·5—217°, from which 9 : 9 : 10-triphenyldihydroanthracene, m. p. 226—227°, is obtained by treatment with HCl in boiling AcOH.

Tetraphenyl-o-xylylene glycol does not react with *iso*amyl nitrite or Me orthosilicate, but is transformed by Et or Bu borate into the *Et* ester

$$C_6H_4 \begin{matrix} CPh_2 \cdot O \\ CPh_2 \cdot O \end{matrix} > B \cdot OR \quad (R=Et), \text{ m. p. } 201—202·5°$$

after softening, or *Bu* ester (R=Bu), m. p. 161—162°, hydrolysed by alkali to the glycol and converted by acid into tetraphenylphthalane; treatment of the ester with K–Na gives a mixture of the compounds $C_6H_4(CPh_2K)_2$ and $CPh_2K \cdot C_6H_4 \cdot CPh_2 \cdot O \cdot B(OR) \cdot OK$, from which 2-hydroxybenzhydrylbenzhydrylbenzene is obtained by alcoholysis (isolated as triphenyldihydroanthracene).

Tetraphenyl-o-xylylene glycol cannot be converted into its Me_2 ether by the use of CPh_3K or K phenyl diphenylyl ketone, which yield only the K_1 compound, whereas K 2-phenyl*iso*propyl affords the K_2 compound, transformed by MeI into *di(methoxybenzhydryl)benzene*, m. p. 179·5—180·5°, which is unexpectedly unstable. It is quant. decomposed by Na–K in dioxan into KOMe and $C_6H_4(CKPh_2)_2$ and converted by EtOH into *tetraphenyl-o-xylene*, m. p. 146·5°. K is eliminated by tetramethylethylene bromide, but, even at −50°, the expected di-radical becomes isomerised to 9 : 9 : 10-triphenyl-9 : 10-dihydroanthracene. Dry O_2 transforms the K compound into a mixture of substances which do not liberate I from HI and from which only triphenyldihydroanthracene could be isolated. H. WREN.

Apparatus for pyrolytic production of diphenyl. A. W. HIXSON, L. T. WORK, H. V. ALESSANDRONI, G. E. CLIFFORD, and G. A. WILKENS (Ind. Eng. Chem. [Anal.], 1931, **3**, 289—291).—C_6H_6 is vaporised at 500° and passed through a steel tube immersed in molten Pb. The optimum temp. for the production of Ph_2 is about 740°. The conversion of C_6H_6 into Ph_2 decreases with increase in the rate of flow; the decrease is not so marked at atm. pressure as at higher pressures. Increased pressure causes better conversion at all rates of flow. H. BURTON.

Diphenyl and its derivatives. VIII. New 2 : 2′-disubstituted derivatives. L. MASCARELLI and D. GATTI (Atti R. Accad. Lincei, 1931, [vi], **13**, 887—893).—The following 2 : 2′-derivatives of diphenyl were prepared according to the scheme $NO_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NO_2 \longrightarrow NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NO_2 \longrightarrow C_6H_4X \cdot C_6H_4 \cdot NO_2 \longrightarrow C_6H_4X \cdot C_6H_4 \cdot NH_2 \longrightarrow C_6H_4X \cdot C_6H_4X$ (X=halogen) : *nitrochloro-*, m. p. 71°; *nitrobromo-*, m. p. 66—67°; *nitroiodo-*, m. p.

81—82°; *nitrohydroxy-* (*Ac* derivative, m. p. 102°); *chloroamino-*, m. p. 56—57°; *bromoamino-*, m. p. about 46—50°; *iodoamino-* (*Ac₂* derivative, m. p. 129—130°); *chloroiodo-*, m. p. 63—64°; *chlorobromo-*, m. p. 58°; *bromoiodo-*, m. p. 90°. T. H. POPE.

Diphenylene sulphide series. C. COURTOT and CHAIX (Compt. rend., 1931, **192**, 1667—1669).—Alkali fusion at 250° of diphenylenesulphone or its substituted derivatives yields the corresponding diphenyl - 2 - sulphonic acid (*diphenyl - 2 - sulphonyl chloride*, m. p. 103°; *sulphonamide*, m. p. 120·5°; *dibromodiphenyl-2-sulphonyl chloride*, m. p. 93·5—94·5°; *sulphonamide*, m. p. 151—152°), hydrolysed by aq. HBr to the diphenyl (3 : 3′-*dibromodiphenyl*, m. p. 52·5—53°). G. DISCOMBE.

Polyphenyls. I. *sym.*-Diphenyldiphenyls. S. T. BOWDEN (J.C.S., 1931, 1111—1114).—When 2- or 3-iododiphenyl is heated with Cu-bronze at 255—260°, 2 : 2′-, m. p. 118—119°, and 3 : 3′, m. p. 86°, -*diphenyldiphenyl*, respectively, are obtained. 4 : 4′-Diphenyldiphenyl may be similarly prepared, but is best obtained (63% yield) by heating anhyd. $CuCl_2$, activated Mg, and 4-bromodiphenyl at 100°. It is also obtained in small yield by pyrolysis of Ph_2. J. W. BAKER.

Stereochemical studies on hydronaphthalenes and derivatives. II. Catalytic oxidation–reduction of hydronaphthalenes and sesquiterpenes. S. KIMURA.—See this vol., 1288.

4 : 4-Derivatives of diphenyldidiphenylyl and didiphenylyl. R. PUMMERER and L. SELIGSBERGER (Ber., 1931, **64**, [B], 2477—2486; cf. A., 1924, i, 381).—4 : 4′-Di-iododiphenyl and Ag powder at 240—250° give 4-iododiphenyl, unchanged material, a little didiphenylyl (4 : 4′-diphenyldiphenyl), and possibly a trace of diphenyldidiphenylyl. With Cu powder at 250° the I_2-derivative affords Ph_2, *p*-iododiphenyl, didiphenylyl, and diphenyldidiphenylyl. 4 : 4′-Di-iododiphenyl and 4-iododiphenyl with Ag powder at 280—300° give much Ph_2, I-compounds, and very impure $(C_6H_4Ph)_2$ and by Cu powder at 250—275° into Ph_2, $(C_6H_4Ph \cdot)_2$, and $Ph[C_6H_4]_4Ph$, m. p. 465° after softening at 435° (yield 24·4%). 4′-Iodo-4-methyldiphenyl, 4 : 4′-di-iododiphenyl, and Cu powder at 280—300°/200—300 mm. yield Ph_2, impure dimethyldidiphenylyl, and 4‴ : 4⁗-*dimethyldiphenyldidiphenylyl*, m. p. 469° after softening at 435°. 4′-Iodo-4-methyldiphenyl and Ag powder at 300° give 4-methyldiphenyl, m. p. 51°, whereas with Cu powder at 220°, 4″ : 4‴-*dimethyldidiphenylyl*, m. p. 334°, is obtained in 60—70% yield. It is oxidised by CrO_3 in boiling AcOH to 4″-*methyldidiphenylyl-4‴-carboxylic acid*, darkening without melting at 425° (*pyridine* compound; *Na* salt), and *didiphenylyl-4″ : 4‴-dicarboxylic acid*, decomp. 450° (*Na* salt; Me_2 ester, decomp. 325—330°), which yields $(C_6H_4Ph \cdot)_2$ when heated at 500°/18 mm. or (with carbon and other products) when heated in boiling quinoline. 4-*Iododiphenyl-4′-carboxylic acid*, decomp. above 250° (*Na* salt unchanged below 400°), is prepared by oxidation of 4-iodo-4′-methyldiphenyl or from 4-*iododiphenyl-4′-nitrile*, m. p. 166° (from 4-iodo-4′-aminodiphenyl), and subsequent hydrolysis with conc. HCl in Et_2O. *Me 4-iododiphenyl-4′-*

carboxylate, m. p. 189°, is transformed by Cu powder at 270° into Me didiphenylyl-4″ : 4‴-dicarboxylate. H. WREN.

Tribromonaphthalene obtained in bromination of naphthalene. J. S. SALKIND and M. V. BELIKOVA (J. Gen. Chem. Russ., 1931, **1**, 430—436).—Bromination of 1 : 4-dibromonaphthalene gives 1 : 4 : 6-tribromonaphthalene; similarly a SO₃H group takes the 6-position. A NO₂-group takes the 5-position. No clear explanation of this is available. E. B. UVAROV.

Relative ease of formation of rings. III. New synthesis of chrysene. J. VON BRAUN and G. IRMISCH (Ber., 1931, **64**, [*B*], 2461—2465; cf. A., 1929, 561).—*meso*-βγ-Diphenyladipic acid (cf. Oommen and Vogel, A., 1930, 1435) is transformed by SOCl₂ into the corresponding chloride, which, with AlCl₃ in CS₂ or light petroleum, slowly affords 4-*keto-2-phenyl-1 : 2 : 3 : 4-tetrahydronaphthyl-1-acetic acid*, m. p. 148° (*semicarbazone*, m. p. 225°), and the *ketone*

$$CO < {CH_2-CH \cdot C_6H_4 \atop C_6H_4 \cdot CH-CH_2} > CO \text{ (I), m. p. 295° after soften-}$$

ing at 285°. Treatment of the ketone according to Clemmensen in presence of EtOH gives Et *meso*diphenyladipate, m. p. 114°, also obtained by use of EtOH and HCl in absence of Zn, but not from 4-keto-2-phenyl-1 : 2 : 3 : 4-tetrahydronaphthyl-1-acetic acid under analogous conditions. Reduction of the *meso*-ketone with P and HI at 170—180° gives the non-homogeneous *hydrocarbon* [as (I), but H₂ for O], dehydrogenated by PbO to chrysene, m. p. 248°. *r*-Diphenyladipyl chloride with AlCl₃ yields *r*-diphenyladipic acid, very little 4-keto-2-phenyl-1 : 2 : 3 : 4-tetrahydronaphthyl-1-acetic acid, and the *r*-*diketone* (cf. I), m. p. 182—184° (*semicarbazone*, m. p. 305°), converted by amalgamated Zn and HCl into a complex hydrocarbon. Reduction of the diketone by P and HI gives the *r*-*hydrocarbon*, b. p. about 140°/0·5 mm., m. p. 50—55°, dehydrogenated by PbO to chrysene. H. WREN.

Polycyclic aromatic hydrocarbons. VII. 5 : 6-*cyclo***Penteno-1 : 2-benzanthracene, a cancer-producing hydrocarbon.** J. W. COOK (J.C.S., 1921, 2529—2532).—The ketone formed from the interaction of hydrindene, 2-methyl-1-naphthoyl chloride, and AlCl₃ when heated gives a mixture of 5 : 6-*cyclo*penteno-1 : 2-benzanthrene (this vol., 612) (*picrate*, m. p. 195°; quinone, m. p. 184·5—185·5°), and (?) 6 : 7-cyclo*penteno-1 : 2-benzanthracene*, m. p. 164—165° (*quinone*, m. p. 182—184°), purified through the *picrate*, m. p. 180°. 1 : 2 : 5 : 6-Dibenzanthraquinone or 5 : 6-*cyclo*penteno-1 : 2-benzanthraquinone on oxidation with KMnO₄ in hot H₂SO₄ gives *anthraquinone-1 : 2 : 5 : 6-tetracarboxylic acid*, m. p. >360°, purified through the *Me₄ ester*, m. p. 292—293°, which is obtained from the Ag salt. A. A. LEVI.

Coloured hydrocarbons. Violet hydrocarbon, C₃₆H₂₂. C. DUFRAISSE and M. BADOCHE (Compt. rend., 1931, **193**, 529—531).—C₃₆H₂₄ (this vol., 1151) with NaOEt gives a violet *hydrocarbon*, C₃₆H₂₂, m. p. 270—271°, considered to be phenylenediphenyldibenzbifulvene. The absorption spectrum was measured. A. A. LEVI.

Aniline and methyl chloride. W. D. BANCROFT and B. C. BELDEN (J. Physical Chem., 1931, **35**, 3090—3091).—MeCl and NH₂Ph react slowly at room temp. yielding mainly NHPhMe,HCl and a trace of a magenta-coloured dye. Below 180°, MeCl and dry biuret do not react. L. S. THEOBALD.

Condensation of ethyl propylacetoacetate with aromatic amines. I. G. V. JADHAV (J. Indian Chem. Soc., 1931, **8**, 681—684).—When Et *n*-propylacetoacetate is heated with NH₂Ar, a mixture of the carbamide CO(NHAr)₂ and the anilide CHPrAc·CO·NHAr is usually produced; long heating favours carbamide formation. The following are new : n-*propylacetoacet-anilide*, m. p. 96—97°; -*o*-, m. p. 105—106°, and -*p*-, m. p. 112—113°, -*toluidides*; -*p-anisidide*, m. p. 115°; -*p-phenetidide*, m. p. 115°; -*m*-4-*xylidide*, m. p. 100—101°; -*p-xylidide*, m. p. 113—114°. *s-Di*-m-4- and *s-di*-p-*xylylcarbamides* have m. p. 239—240° and above 275°, respectively. H. BURTON.

Polysulphides of arylthiocarbimides. T. G. LEVI (Gazzetta, 1931, **61**, 619—622).—Previous work on sulphides of arylthiocarbimides is discussed. The *hexasulphides* of phenyl- (m. p. 80—90°), *o*-tolyl-, and *p*-tolyl-thiocarbimides are obtained by the action of S₂Cl₂ on the NH₄ aryldithiocarbamates. E. E. J. MARLER.

Polymorphism. II. Further researches on *o*-nitroaniline. N. H. HARTSHORNE and A. STUART (J.C.S., 1931, 2583—2591).—A third form, γ, of *o*-nitroaniline has been identified (cf. A., 1930, 764) and is apparently the most stable; it is that described by von Jaeger (Z. Krist., 1905, **40**, 114) and by Herrmann and Burak (A., 1929, 18). It has been prepared by stabilisation of the β-form on microscope slides, has m. p. 71·2—71·3°, and is monoclinic. Both α- and β-forms are also monoclinic, and optical properties for each of the forms have been determined. The β-form is preferentially deposited from a melt. F. R. SHAW.

Steric hindrance. V. J. VON BRAUN and W. RUDOLPH (Ber., 1931, **64**, [*B*], 2465—2473; cf. A., 1930, 466).—The different behaviour of an *o*-substituent in Ar in the reactions Ar·NHR+ClX = Ar·NR·X+HCl and Ar·NMe₂+MeI = Ar·NMe₃I is explained by a consideration of electrochemical as well as steric factors. In a compound I and II the electrochemical character of X as well as its steric effect on
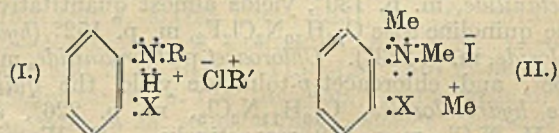
the mobility of H (I) and the additive power of the *tert.*-N (II) must be considered. In (I) a negative X (Cl, Br) attracts the positive H into its field more powerfully and renders it less reactive with ClR′ than does a positive X (Me); in (II) the influence of X on the Me of MeI is similar, *i.e.*, the final effect is that Cl or Br afford less "steric hindrance" than Me. In conformity with these views it is shown that *o*-fluorodimethylaniline adds MeI with great readiness, whereas *o*-fluoroimido-chlorides are very stable, and that strongly electronegative substituents make their

presence felt in the *m-* but not in the *p*-position, whereas the weakly positive Me group has scarcely any action.

The reaction of the Ac and chloroacetyl derivatives of the amines with PCl_5 is effected by admixture at $\not> 20°$ and keeping the Ac compounds for 3 hr. at 20° and for 1 hr. at 65°, and of the chloroacetyl compounds for 16 hr. at 20° and for $\frac{1}{2}$ hr. at 60°. The following compounds are described : o-*fluorodimethylaniline*, b. p. 64—65°/13 mm. (*picrate*, m. p. 131°; *methiodide*, decomp. 21°), transformed by CH_2O into 2-*fluoro-4-hydroxymethyldimethylaniline*, b. p. 115—120°/0·1 mm. (*picrate*, m. p. 125°; *methiodide*, m. p. 110°); o-*fluoroacetanilide*, m. p. 80°, b. p. 140—142°/14 mm., converted into the *imide chloride* $C_6H_4F\cdot N\colon CMeCl$, b. p. 70°/0·25 mm.; the *amidine* base $C_6H_4F\cdot N\colon CMe\cdot N(C_6H_4F)\cdot CCl\colon CH_2$, m. p. 85° (non-cryst. *hydrochloride*); o-*fluorochloroacetanilide*, b. p. 150—151°/14 mm., m. p. 87°, and the *imide chloride* $C_6H_4F\cdot N\colon CCl\cdot CH_2Cl$, b. p. 83—85°/0·2 mm.; m-*fluoroacetanilide*, m. p. 88°, converted by PCl_5 into the corresponding *imide chloride*, b. p. 70°/0·25 mm., and, mainly, the *amidine*, $C_{16}H_{13}N_2ClF_2$, m. p. 74°; m-*fluorochloroacetanilide* and the corresponding *imide chloride*, b. p. 112—115°/0·55 mm., and the quinoline *base*, $C_{16}H_{10}N_2Cl_2F_2$, m. p. 186° (*hydrochloride*, decomp. 216° after darkening at 206°); the quant. behaviour of chloroacet-*m*-chloroanilide is described (cf. this vol., 236); chloroacet-m-*toluidide*, m. p. 88°, b. p. 154°/0·2 mm., and the *quinoline hydrochloride*, $C_{18}H_{17}N_2Cl_3$, m. p. 214°.

3-Nitro-*o*-toluidine is transformed through the corresponding *diazonium fluoborate*, decomp. 143° after softening at 120°, into 2-*fluoro-3-nitrotoluene*, b. p. 110—111°/12 mm., reduced by $SnCl_2$ to 2-*fluoro*-m-*toluidine*, b. p. 85—87°/12 mm. (*picrate*, m. p. 205°; *hydrochloride*, m. p. 197°). The *Ac* derivative, b. p. 167—170°/14 mm., is converted by PCl_5 into the *imide chloride*, C_9H_9NClF, b. p. 97°/high vac., and, mainly, the *chlorovinylamidine*, $C_6H_3MeF\cdot N\colon CMe\cdot N(CHCl\colon CH_2)\cdot C_6H_3MeF$, m. p. 90° (non-cryst. *hydrochloride*). The Ac derivative of *vic*-*o*-xylidine yields the corresponding *imide chloride*, b. p. 108—110°/3 mm., and the *chlorovinyl* base, $C_{20}H_{23}N_2Cl$, m. p. 94° (non-cryst. *hydrochloride*). *p*-Fluoroacet-anilide affords essentially the *chlorovinyl* base, $C_{16}H_{13}N_2ClF_2$, m. p. 101°, and a little imide chloride due probably to incomplete reaction. p-*Fluorochloro-acetanilide*, m. p. 130°, yields almost quantitatively the quinoline *base* $C_{16}H_{10}N_2Cl_2F_2$, m. p. 152° (*hydro-chloride*, m. p. 233°). *Chloroacet*-p-*chloroanilide*, m. p. 168°, and chloroacet-*p*-toluidide yield the *quinol-ine hydrochlorides*, $C_{16}H_{11}N_2Cl_5$, m. p. 226°, and $C_{18}H_{17}N_2Cl_3$, m. p. 270, respectively. H. WREN.

Affinity of organic residues. VIII. J. VON BRAUN, W. MAY, and R. MICHAELIS (Annalen, 1931, **490**, 189—200).—The relative strengths of attachment of the CH_2Ph residue in the substituted dibenzylmethylamines and dibenzyl sulphides are determined by the nature of the fission products with CNBr of substances containing two different radicals (cf. A., 1926, 1231); in both series the order of increasing affinity is : *p*-methylbenzyl, benzyl, *m*-methyl-benzyl, *o*-methylbenzyl, and in the methylamine series

p-methoxybenzyl, *p*-phenylbenzyl, *m*-methylbenzyl. The required substituted dibenzylmethylamines are separated by distillation from the mixture produced by combination of a benzylmethylamine with the benzyl chloride. For the prep. of the substituted dibenzyl sulphides a substituted benzyl chloride is treated with NH_4 dithiocarbamate in EtOH, the thio-urethane produced hydrolysed by alkali, and the resulting mercaptan condensed with the second benzyl chloride. The following are described and appear to be new : p-*methyl*-, b. p. 82—84°/11 mm. (*picrate*, m. p. 145°; *hydrochloride*, m. p. 174°), and m-*methyl-benzylmethylamine*, b. p. 86—88°/12 mm. (*picrate*, m. p. 133°; *hydrochloride*, m. p. 149°); 3 : 4′-*di-methyl*-, b. p. 173—175°/12 mm. (*methiodide*, m. p. 189°), 2 : 3′-*dimethyl*-, b. p. 173—175°/11 mm. (*methiodide*, m. p. 175°), 2 : 4′-*dimethyl*-, b. p. 178—180°/14 mm. (*methiodide*, m. p. 207°), 3-*methyl*-, b. p. 162—163°/11 mm., 4-*methoxy*-, b. p. 187—189°/14 mm., 2-*methyl*-, b. p. 164—166°/10 mm. (*methiodide*, m. p. 199°), 4-*methoxy-4′-methyl*-, b. p. 195—198°/15 mm., and 4-*methoxy-4′-phenyl-dibenzylmethylamine*, b. p. 222—224°/0·6 mm.; m-*methylbenzyl*-, b. p. 158—160°/11 mm., p-*methylbenzyl*-, b. p. 156—158°/13 mm., and *diphenylyl-methylcyanamide*, b. p. 218—220°/11 mm.; m-*methylbenzyl*-, m. p. 175°, and *anisyl*-, m. p. 142°, *-trimethylammonium bromides*; 2-*methyl*-, m. p. 177°, 3 : 3′-*dimethyl*-, m. p. 183°, 4 : 4′-*dimethoxy*-, m. p. 205°, and 4 : 4′-*dimethoxy-4″-methyl*-, m. p. 100—105° (impure ?), *-tribenzylmethylammonium brom-ides*; p-*methyl*-, m. p. 104°, and m-*methyl-benzyldi-thiourethane*, m. p. 68°; p-*methyl*-, b. p. 89—90°/11 mm., and m-*methyl-benzyl mercaptan*, b. p. 90°/12 mm. (*disulphides* oily in both cases); 2 : 3′-, 2 : 4′-, and 3 : 4′-*dimethyl*-, and 3-, and 2-*methyl-dibenzyl sul-phides*; *benzyl*, b. p. 120—122°/14 mm., and o-, b. p. 148—150°/15 mm., and m-*methylbenzyl thiocyanate*, b. p. 148—150°/14 mm.; p-, m. p. 92°, and m-*methylbenzyl β-naphthyl ether*, m. p. 85°. *Anisyl-idenebenzylamine*, b. p. 216°/12 mm., is reduced by Na and EtOH to 4-*methoxydibenzylamine*, b. p. 206°/12(?) mm. (*hydrochloride*, m. p. 213°; *picrate*, m. p. 120°; *Bz* derivative, m. p. 65°). The Bz derivative is con-verted by PCl_5 (1 mol.) at 115—120° into benzyl-benzamide and anisyl chloride (4-*methoxydiphenyl-amine*, m. p. 65°). H. A. PIGGOTT.

Ditolyl series. II. Resolution into optical antipodes of *dl*-2-nitro-2′-amino-6 : 6′-dimethyl-diphenyl. A. ANGELETTI [with P. GUALA] (Gaz-zetta, 1931, **61**, 651—656).—Reduction of 2 : 2′-dinitro-6 : 6′-dimethyldiphenyl with NH_4HS gives 2-*nitro-2′-amino*-6 : 6′-*dimethyldiphenyl*, m. p. 122—123°, which is resolved by combination with *d*-tartaric acid, giving the d-*tartrates* of l-, $[\alpha]_D^{20}$ —40°, and d-2-*nitro-2′-amino*-6 : 6′-*dimethyldiphenyl*, $[\alpha]_D^{20}$ +40. The base is not easily racemised. E. E. J. MARLER.

Derivatives of naphthalene-2-sulphonic acid. F. FABROWICZ and W. LEŚNIAŃSKI (Rocz. Chem., 1931, **11**, 636—654).—4-*Benzeneazo-α-naphthylamine*-6- and -7-*sulphonic acids* yield on treatment in NaOH solution with $NaHSO_3$ 1 : 4-*diaminonaphthalene*-6- and -7-*sulphonic acids*, the former of which is oxidised by HNO_3 to 1 : 4-*naphthaquinone*-6-*sulphonic acid*. 1-Nitronaphthalene-6- and -7-sulphonic acids, m. p.

118—119° and 135—136°, respectively, yield on reduction with $(NH_4)_2S$ 1-*hydroxylaminonaphthalene*-6- and -7-*sulphonic acids*, whilst on treatment with NH_4HS followed by conc. HCl 4-*amino*-α-*naphthol*-6- and -7-*sulphonic acids* are obtained. These yield 4-*diazo*-α-*naphthol*-6- and -7-*sulphonic anhydrides* on treatment with Et nitrite, whilst on oxidation with conc. HNO_3 1 : 4-*diazonaphthol*-6- and -7-*sulphonic acids* are produced. Reddish-brown dyes are obtained by diazotising the above aminosulphonic acids and coupling with β-naphthol.   R. Truszkowski.

Effect of the lactonic ring on the colour of azo-dyes. D. Chakravarti (J. Indian Chem. Soc., 1931, 8, 503—509).—Azo-derivatives of coumaric acid, although approx. the same colour as the corresponding coumarin derivatives, have a much greater affinity than the latter for fibres. The following dyes were prepared either by coupling diazotised arylamines with coumarin in NaOH solution, or by coupling diazotised 6-aminocoumarin (modified prep. from 6-nitrocoumarin, m. p. 185°) with phenols or coumarin derivatives in NaOH solution : 6-*azocoumarin*, yellow, m. p. above 300°; *coumarinazo*-o-*coumaric acid*, light brown, decomp. 177°; *azo*-o-*coumaric acid*, reddish-brown, m. p. above 300°; *coumarinazo*-4 : 7-*dimethyl-coumarin*, greenish-yellow, m. p. 280°; *coumarinazo*-4 : 6-*dimethylcoumarin*, golden-yellow, m. p. 262°; *coumarinazo*-4-*methyl*-α-*naphthacoumarin*, orange, m. p. above 280°; *coumarinazo*-7-*hydroxy*-4-*methylcoumarin*, softening at 205°; *coumarinazo*-7 : 8-*dihydro*-4-*methyl-coumarin*, brownish-black, softening at 282°; *coumarinazoresorcinol*, reddish-brown, m. p. 245°; *coumarinazodimethylaniline*, reddish-yellow, m. p. 231°; 8-p-*nitrobenzeneazo*-6-*iodocoumarin*, reddish-brown; *coumarinazo*-6-*iodocoumarin* (I), brown; 8-*coumarinazo*-6-*aldehydocoumarin* (II), brown; p-*nitro-benzeneazo*-7 : 8-*dihydroxy*-4-*methylcoumarin*, brown, softening at 292°. The colours developed on silk and wool are given for the above compounds and for benzene-, o-, m-, and p-nitrobenzene-, naphthalene-α- and -β-azocoumarin, diphenylbisazodicoumarin, benz-eneazo-4 : 6-dimethylcoumarin, and the corresponding coumaric acids. Coumaric acids could not, however, be obtained from the azodimethylcoumarins. The acids from (I) and (II) probably exist in the quinonoid form. 6-Nitrocoumarin does not form azo-compounds.   R. S. Cahn.

Attempts to prepare dyes from fluorenone. A. C. Sircar and K. C. Bhattacharyya (J. Indian Chem. Soc., 1931, 8, 637—643).—Fluorenone-2-di-azonium chloride couples with the following substances yielding *azo*-compounds (m. p. given in parentheses) which dye wool evenly from a 1% H_2SO_4-bath in shades varying from orange-yellow to scarlet and bluish-violet : β-naphthol (192—194°); PhOH (213°); NMe₂Ph (193°); NEt₂Ph (above 310°); salicylic acid (216°); 3-hydroxy-β-naphthoic, naphthionic, α-naphthol-4-sulphonic, and β-naphthol-3 : 6- and -6 : 8-disulphonic acids (all above 310°). *Arylidene*-2-*aminofluorenones*, prepared from 2-aminofluorenone (I) and the requisite araldehyde (usually in EtOH), are not satisfactory dyes; the following are described : *benzylidene*, m. p. above 290°; o-, m. p. 230°, m-, m. p. above 290°, and p-, m. p. above 290°, -*hydroxybenzyl-*

idene; o-, m. p. 152°, m-, m. p. 213°, and p-, m. p. above 290°, -*nitrobenzylidene*; p-*acetamidobenzylidene*, m. p. above 290°; p-*dimethylaminobenzylidene*, m. p. 256°; 2 : 4-*dihydroxybenzylidene*, m. p. above 290°, and 4-*hydroxy*-3-*methoxybenzylidene*, m. p. above 290°. 2-*Oxamido*-, -*phthalamido*-, -*malonamido*-, -*succin-amido*-, and -*glutaramido-fluorenones*, all not melted at 290°, are obtained from 2 mols. of (I) and 1 mol. of the requisite acid chloride in $PhNO_2$. s-*Di*-2-*fluorenonyl-carbamide* and -*thiocarbamide*, both m. p. above 290°, were prepared. None of these amides gives a sol. vat when reduced with hyposulphite.   H. Burton.

Chemical reactions induced by light. II. C. Piccinini and L. Vecchiotti (Gazzetta, 1931, 61, 626—630; cf. A., 1930, 1180).—In a mixture of $PhNO_2$ and NH_2Ph exposed to sunlight for 5 months, azoxybenzene, o-hydroxyazobenzene, and traces of p-aminophenol are detected. The action is not due to the sun's heat and does not occur when luminous radiations are excluded.   E. E. J. Marler.

p-Alkylsulphonylphenylhydrazines. E. Koe-nigs and A. Wylezich (J. pr. Chem., 1931, [ii], 132, 24—38).—p-Bromothiophenol is alkylated and the product oxidised by H_2O_2 to the sulphone, the Br in which is readily replaced by action of N_2H_4 in EtOH at 100—120°. The following are described : p-bromophenyl, methyl, *ethyl*, m. p. 56—57°, n-*propyl*, m. p. 52—53°, iso*propyl*, m. p. 67°, n-*butyl*, m. p. 61°, iso*butyl*, m. p. 49°, n-*hexyl*, m. p. 49°, *benzyl*, m. p. 159°, and *phenylethyl*, m. p. 86—87°, *sulphones*; p-*methyl*-, m. p. 135—136° (*benzylidene* derivative, m. p. 206—208°; indefinite compounds, m. p. 155—176°, with dextrose), p-*ethyl*-, m. p. 112—113°, p-n-*propyl*-, m. p. 104—105°, p-iso*propyl*-, m. p. 110—111°, p-n-*butyl*-, m. p. 139—140°, p-iso*butyl*-, m. p. 127—128°, p-iso*amyl*-, m. p. 143°, p-n-*hexyl*-, m. p. 125—126°, p-*phenyl*-, m. p. 202—203°, p-*benzyl*-, and p-*phenylethyl*-, m. p. 144—145°, -*sulphonylphenyl-hydrazines*; *methylenedi*-p-*bromophenyl sulphide*, m. p. 77°, *sulphone*, m. p. 209—210°; s-*ethylenedi*-p-*bromo-phenyl sulphide*, m. p. 177°, *sulphone*, m. p. 271—272°; s-*pentamethylenedi*-p-*bromophenyl sulphide*, m. p. 70—71°, *sulphone*, m. p. 151°. The disulphones did not react normally with N_2H_4 to give the hydrazine; in the case of the ethylene compound fission to p-methylsulphonylphenylhydrazine occurred.
   H. A. Piggott.

m-Phenylenedihydrazine. H. Wieland, D. Juchum, and J. Maier (Ber., 1931, 64, [B], 2513—2516).—Resorcinol is converted by N_2H_4 pyro-sulphite and N_2H_4,H_2O at 115—120° into m-*phenyl-enedihydrazine*, m. p. 124° (decomp.), stable when dry but unstable in aq. solution [*hydrochloride*; *sulphate*; *oxalate*, decomp. 138°; *dibenzylidene*, m. p. 254°, Ac_2 m. p. 227° (decomp. after darkening at 222°), Bz_2, decomp. 225°, derivatives; *disemicarbazide*, decomp. 272°]. Attempts to prepare compounds with a 10-membered hetero-ring were unsuccessful. With CH_2Ac_2, m-phenylidenedihydrazine affords m-*phenylene*-1 : 1'-*di*-3 : 5-*dimethylpyrazole*,

$$C_6H_4 \cdot \left(N \underset{CMe:CH}{\overset{N=CMe}{<}}\right)_2, \text{ m. p. } 106°. \quad \text{H. Wren.}$$

Aromatic diazo-compounds. III. H. T. Buc-herer and A. Fröhlich (J. pr. Chem., 1931, [ii], 132,

72—112).—Yellow-II (A., 1930, 1280; cf. Rowe etc., A., 1926, 625), the formation of which from yellow-I, the isomeride obtained by the action of KOH on p-nitrobenzenediazonium β-naphthol-1-sulphonate is discussed, can be esterified (*Et* ester, m. p. 179°) and benzoylated (*Bz* derivative, $C_{23}H_{17}O_6N_3$, m. p. 129°), and reduced to the corresponding NH_2-compound (III), m. p. 231°, without affecting the rest of the mol.; it does not, therefore, appear to contain the diazo-group. A crude reduction product of yellow-I gives (III) with HCl, and on diazotisation and coupling with R-salt gives a reddish-blue dye, converted into the red dye from (III) by HCl. The *substance*, m. p. 229° (IV), obtained by heating yellow-II with HCl at 150° is the simple decarboxylated derivative, and is free from phenolic groups; the corresponding NH_2-compound, m. p. 255°, is obtained both from (III) and HCl and from (IV) by reduction. Yellow-II is decomposed completely by 20% KOH at 150° under pressure, but at the b. p./1 atm. azobenzene, benzidine, NH_2Ph, phthalic acid, and 1 at. proportion of N_2 are produced; distillation with Zn dust gives NH_3 and NH_2Ph, and oxidation with alkaline $KMnO_4$ gives phthalic acid. More drastic conditions are needed for the fission of (III), which with boiling 80% KOH gives p-phenylenediamine, NH_3, and phthalic acid.

The action of weak acids in aq. solution (*e.g.*, $NaHCO_3$, H_2CO_3, H_3BO_3, AcOH, and dil. $H_2C_2O_4$) on the *anti*-diazotate of p-nitroaniline leads first to formation of the *syn*-diazotate, which apparently is partly hydrolysed to HNO_2 and p-nitroaniline, the NO_2-group being simultaneously replaced by OH; the products are 4 : 4'-dinitrodiazoaminobenzene, p-hydroxydiazobenzene (20%), and HNO_2. The o-NO_2-group is more easily removed, the yield of OH-compound in this case being 50% of theory. The reaction time only, and not the yield, is affected by temp. or pressure conditions, or by the nature of the acid used within the stated limits. An additional negative group in the m-position to the NO_2-group markedly increases the ease of its replacement by OH. Thus almost quant. conversion into OH-compound occurs with 2-nitroaniline-4-sulphonic acid, or with 2 : 4-dinitroaniline in about one twentieth the time taken with o-nitroaniline, the formation of a chromable azo-dye with R-salt in the latter case pointing to replacement of the o-NO_2-group. On the other hand, the *anti*-diazotate from 4-nitroaniline-2-carboxylic acid seems to be stable to $NaHCO_3$. The diazotates from 5- and 6-nitro-o-toluidines react with $NaHCO_3$ only very slowly. With HNO_2 the *syn*-diazotates can undergo both the above-mentioned reactions, and also replacement of the diazo- by the NO_2-group (examples: o-, m-, and p-nitroanilines, p-chloro-aniline, and β-naphthylamine; 2-nitroaniline-4-sulphonic acid is converted mainly into OH-compound).

In spite of the above observations, the dyes obtained by coupling the *anti*-diazotate from p-nitroaniline with J- and γ-acids gave p-phenylenediamine on reduction, and are therefore p-nitro- and not p-hydroxy-azo-dyes. o-Hydroxyazo-dyes from K-acid, as expected, do not couple with this diazotate. The coupling of pyrogallol, salicylic acid, α-naphthol-

3 : 6- and -3 : 8-disulphonic acids, α-naphthylamine-6- and -7-sulphonic acids (mixed), and resorcinol with the *anti*-diazotate proceeds exactly as with p-nitro-benzenediazonium chloride, and gives in most cases a mixture of o- and p-hydroxyazo-dye. Yellow-I is the compound (II) and yellow-II the 1-hydroxy-3-p-nitrophenyl-1 : 3-dihydrophthalazine-4-acetic acid of Rowe etc. (*loc. cit.*). H. A. PIGGOTT.

Reactivity of aromatic hydroxyl groups. II. H. L. BASSETT (J.C.S., 1931, 2516—2518).—The rate of reaction (cf. A., 1930, 1033) of certain halogenated phenols with AcBr in AcOEt increases with acidity of the phenol, with the exception of o- and p-iodo-phenols. The abnormal slowness of the o-substituted compounds may be due to steric hindrance, but it is modified by a p-Me group. F. R. SHAW.

Decomposition of phenol and naphthol ethers by concentrated hydrochloric acid. G. B. KOL-HATKAR and R. P. GHASWALLA (J. Indian Chem. Soc., 1931, **8**, 511—516).—The numbers quoted after the following ethers are the % hydrolysis taking place when the ethers are heated with 10N-HCl at 130° for 2 hr.; the numbers in parentheses and brackets refer to 5N-HCl at 130° and 10N-HCl at 100°, respectively, from 2 hr.: PhOMe, 33; PhOEt, 14·8; m-, o-, and p-nitroanisole, 6·4 (1·3) [1·29], 10·83 (1·95) [1·9], and 12·77 (2·4) [2·3], respectively; m-, o-, and p-chloroanisole, 3·55, 9·9, and 12·8, respectively; m-, o-, and p-bromoanisole, 2·33, 4·67, and 6·3, respectively; m-, o-, and p-tolyl Me ether, 11·4, 12·1, 16·1, respectively; m-, o-, and p-aminoanisole, 12, 35·5, 75 [33·25], respectively; m-, o-, and p-acetyl-anisole, 12, 53·8, 68·3 [8·8], respectively; 2 : 4- and 3 : 5-dinitroanisole, 3·3 and 3·7, respectively; 2 : 4 : 6-tribromoanisole, 3·7; p-nitrophenetole, 5·34; p-chlorophenetole, 6·3; p-bromophenetole, 3·5; p-methylphenetole, 5·4; α-naphthyl Me ether, 15·7; β-naphthyl Me ether, 26·8; ar-tetrahydro-α-naphthyl Me ether, 9·2. p-Nitrophenol can be determined by KBr-$KBrO_3$ mixture in the presence of its Me and Et ethers, since the latter are unaffected by the reagent. Other phenols were determined by bromination after removal of the ethers by Et_2O; this method is, however, inapplicable to m-bromophenol, 2 : 4 : 6-tri-bromophenol, and the aminophenols, and in these cases the undecomposed ether was extracted and weighed. Br, Cl, NO_2, and Me increase, whilst Ac and NH_2 decrease, the stability of the ethers; the order for position isomerides is regularly $p > o > m$; phenetoles are more stable than anisoles. R. S. CAHN.

Synthesis of thyronamine. R. STÖHR (Z. physiol. Chem., 1931, **201**, 142—148).—4-p-Anisyloxy-benzaldehyde (I) was obtained (*a*) from p-bromo-anisole and PhOH by Harington's method (A., 1926, 724), (*b*) from p-bromonitrobenzene and quinol Me ether through the stages 4-p-anisyloxy-nitrobenzene, m. p. 111°, -aniline, m. p. 79° (lit. 81—82°) (*hydro-chloride*, m. p. 212°), -benzonitrile, m. p. 109° (converted into the aldehyde with $SnCl_2$ and HCl by way of the aldimine–$SnCl_4$ additive product). Condensation of (I) with $MeNO_2$ in presence of KOH yields ω-*nitro*-4-p-*anisyloxystyrene* (II), m. p. 79°. Reduction of (II) with Zn dust and AcOH in EtOH

affords the *oxime*, which on reduction with Na–Hg in AcOH and EtOH gives 4-p-*anisyloxyphenylethylamine* (*hydrochloride*, m. p. 221·5°), which when heated with HI yields thyronamine. J. H. BIRKINSHAW.

Orientation in the aromatic ether series. J. REILLY, P. J. DRUMM, and B. DALY (Proc. Roy. Irish Acad., 1931, **40**, B, 90—93).—The product of nitration of phenyl p-tolyl ether is 4 : 2′-dinitro-4′-methyldiphenyl ether, since it is identical with the products of nitration of 4-nitrophenyl p-tolyl ether, or of Ph 3-nitro-p-tolyl ether. The product of nitration of 2-nitrophenyl p-tolyl ether is probably the 2 : 2′-$(NO_2)_2$-derivative. A. A. LEVI.

Sulphur isomerism of benzyl sulphide. O. HINSBERG (Ber., 1931, **64**, [B], 2500—2504; cf. A., 1929, 310, 1269).—The action of 70% $HClO_4$ on α-benzyl sulphide, m. p. 49°, in C_6H_6 yields β-*benzyl sulphide perchlorate*, decomp. 178°, benzyl disulphide, and dibenzyl. The perchlorate is transformed into the *hydrochloride*, m. p. 81°, which rapidly decomposes when preserved into HCl, and a liquid (? β-benzyl sulphide), isomerising to the α-sulphide, m. p. 49°, and the *picrate*, m. p. 140°. The perchlorate is converted by 1% KOH–MeOH slowly at room temp., more rapidly when heated, into the non-cryst. β-*benzyldibenzyl sulphide*, $CH_2Ph·CHPh·S·CH_2Ph$, oxidised through the *sulphoxide* to β-*benzyldibenzylsulphone*, m. p. 122°. Prolonged contact of the perchlorate with 1—2% KOH–EtOH leads to the formation of α-*benzyldibenzyl sulphide*, m. p. 64°, oxidised by H_2O_2 in Ac_2O to the corresponding *sulphone*, m. p. 157°. H. WREN.

Crystalline form of diphenyldiphenylene-ethylene, diphenyldiphenylene-ethylene oxide, and of the " mixed crystals " formed therefrom. O. ZEDLITZ (Ber., 1931, **64**, [B], 2424—2428).—Crystallographic data are recorded for the materials (cf. Schlenk and Bergmann, A., 1928, 1031 *et seq.*; Kliegl, this vol., 1413). The substances represent three differing types of crystal which are assigned to the same class. The expression " mixed crystals " is not justified, since they are not isomorphous mixtures, but probably mol. compounds. H. WREN.

Action of oxalyl chloride on thymol, guaiacol, pyrocatechol, and quinol. J. MIKŠIĆ and Z. PINTEROVIĆ (Glasn. Hem. Društ. Ktal. Jugoslav., 1930, 6 pp.; Chem. Zentr., 1931, i, 2607).—Thymyl oxalate has m. p. 61°; guaiacyl oxalate has m. p. 127°; pyrocatechyl oxalate has m. p. 184°. Quinyl oxalate was not obtained. A. A. ELDRIDGE.

Dinaphthyl derivatives. A. KORCZYŃSKI and T. TUCHOLSKI (Rocz. Chem., 1931, **11**, 655—663).—2 : 2′-Dimethoxy-αα-dinaphthyl yields an oily additive *product* on nitration in AcOH, which on keeping deposits 2 : 2′-*dimethoxy*-4 : 4′-*dinitro*-αα′-*dinaphthyl*, m. p. 244°, which on reduction yields the corresponding $(NH_2)_2$-derivative (Ac_2 derivative, m. p. 256°); this on diazotisation and coupling with H-acid yields a product, the K salt of which ($C_{42}H_{26}O_{10}N_6S_4K_6$) forms colloidal solutions with H_2O. This dye is substantive for cotton, which is dyed a violet colour. R. TRUSZKOWSKI.

Derivatives of 1 : 2 : 3 : 4-tetrahydroxybenzene. I. W. BAKER and H. A. SMITH (J.C.S., 1931, 2542—2549).—2-*Hydroxy*-3 : 4-*dimethoxybenzaldehyde*, (I), m. p. 74° (*phenylhydrazone*, m. p. 156°), obtained from pyrogallol 1 : 2-Me_2 ether by the Gattermann reaction, may be methylated to 2 : 3 : 4-trimethoxybenzaldehyde (*phenylhydrazone*, m. p. 155—156°). Oxidation of (I) with H_2O_2 affords 1 : 2-dihydroxy-3 : 4-dimethoxybenzene (Bz_2 derivative, m. p. 96°), identical with the substance obtained by Ciamician and Silber (A., 1896, i, 608) from dill apiole. It is methylated to 1 : 2 : 3 : 4-tetramethoxy- and methylenated to 1 : 2 - methylenedioxy - 3 : 4 - dimethoxy-benzene (characterised by its Br_2-derivative). Nitration of pyrogallol 1 : 2-Me_2 ether gives 4-*nitro*-, m. p. 102—103° [methylated to the trimethyl compound (II)], and under different conditions to 4 : 6-*dinitropyrogallol* 1 : 2-*dimethyl ether*, m. p. 76°. Reduction of (II) yields 4-aminopyrogallol Me_3 ether, the hydrochloride of which is oxidised to 2 : 3-*dimethoxy*-p-*benzoquinone*, m. p. 66—67°. This is reduced by Zn and AcOH to 2 : 3-dimethoxyquinol (*diacetate*, m. p. 54—56°), which is methylated to 1 : 2 : 3 : 4-tetramethoxybenzene. Reduction of 3-nitroveratrole with Zn gives o-*azoxyveratrole*, m. p. 125—126°, and not the required hydroxylamine. F. R. SHAW.

Configuration of quercitol. H. KILIANI (Ber., 1931, **64**, [B], 2473—2476; cf. Karrer, A., 1926, 398).—Oxidation of quercitol with HNO_3 (*d* 1·38) does not appear to yield mannosaccharodilactone. The main product is K *l*-trihydroxyglutarate, $[\alpha]_D + 8·55°$ in H_2O. Although the formation of *l*-saccharic acid could not be established, the configuration (I) is regarded as proved for quercitol. H. WREN.

Preparation and utilisation of organomagnesium compounds without use of ether. I. Preparation of β-phenylethyl alcohol. P. SCHORIGIN, V. ISSAGULIANZ, A. GUSSEVA, V. OSSIPOVA, and C. POLJAKOVA (Ber., 1931, **64**, [B], 2584—2590).—MgPhCl is prepared by heating Mg turnings with PhCl at 160—165° in an Fe autoclave provided with mechanical stirring; the best yields, 70% calc. on PhCl or 59% calc. on Mg, are obtained by use of 1 g.-atom Mg and 1 mol. of PhCl. Ph_2 is invariably produced in amount increasing with that of PhCl. I accelerates the change without giving better yields, but affords a darker and more compact product; $NPhMe_2$ retards the reaction. The solubility of the product (g. per 100 c.c. calc. as MgPhCl) in $Et_2O + C_6H_6$ (1 : 1), *iso*amyl ether, benzyl Me ether, benzyl Et ether, and C_6H_6 is respectively 17, 16, 14·5, 14, and 3·6. The equilibrium $2MgPhCl \rightleftharpoons MgPh_2 + MgCl_2$ lies towards the right. Dissolution of the MgPhCl in C_6H_6 and cautious addition of ethylene chlorohydrin at ≯ 35°, followed by distillation of the solvent, affords $CH_2Ph·CH_2·OH$ in 53% yield. Substitution of ethylene oxide in C_6H_6 for the chlorohydrin gives $CH_2Ph·CH_2·OH$ in 70% yield; separation of the product from Ph_2 is effected by treatment with $CaCl_2$ in C_6H_6. H. WREN.

Reduction of aromatic carbinols. A. VANSCHEIDT and B. MOLDAVSKI (J. Gen. Chem. Russ.,

1931, **1**, 304—324).—The reduction of aromatic carbinols by $SnCl_2$ and HI is shown to proceed in two stages : $CR_3 \cdot OH + 2HI \longrightarrow CHR_3 + I_2 + H_2$; $I_2 + SnCl_2 + 2HCl \longrightarrow 2HI + SnCl_4$. Polyarylmethanes are produced in the cases of $CPh_3 \cdot OH$, diphenyl-α-naphthylcarbinol, phenylxanthenol, $CHPh_2 \cdot OH$, fluorenol, and others. Reduction of phenylfluorenol gives diphenyldidiphenylene-ethane. On continued boiling phenylfluorene is formed. Xanthhydrol gives dixanthyl. 9-Alkylfluorenols are unstable in presence of acids and of $SnCl_2$, but a mixture of $SnCl_2$ and HI in acetic acid reduces them, giving dimerides of the radicals, viz., *didiphenylenedimethylethane*, m. p. 209°, *didiphenylenediethylethane*, m. p. 210° (corr.), *didiphenylenedibenzylethane*, m. p. 203—203·5° (corr.). Reduction of phenylfluorenol with HI alone in the cold gives unstable fluorenyl iodide, giving difluorenyl on heating. Excess of HI reduces this to phenylfluorene. In the case of 9-ethylfluorenol an intermediate stage is the formation of ethylidenefluorene. In the reduction of alkylfluorenols dehydration is probably an intermediate stage. E. B. UVAROV.

Constitution of cholesterol. II. Metacholesterol. R. DE FAZI (Gazzetta, 1931, **61**, 630—635). —A new method of obtaining metacholesterol by the action of $CuSO_4$ on cholesterol is described. The work of Lifschütz (A., 1919, i, 591) is confirmed. Metacholesterol is formed when cholesterol is exposed to ultra-violet radiation, but Lifschütz' view that the antirachitic properties of irradiated chlolesterol are due to this is disputed. It is reconverted into cholesterol by KOH–EtOH. Its Br_2 (m. p. 96—97·5°) and Ac (m. p. 112—113°) derivatives are described. The latter may be the Ac derivative of cholesterol. Oscillation of the double linking in cholesterol is suggested to account for its transformation into metacholesterol. E. E. J. MARLER.

Attempted use of the Friedel–Crafts reaction with unsaturated compounds. H. WIELAND and C. HASEGAWA (Ber., 1931, **64**, [B], 2516—2522).— Attempts to apply the Friedel–Crafts reaction to the synthesis of unsaturated ketones are not successful, probably owing to the sensitiveness of the ketones to $AlCl_3$. Cholesterol, AcCl, and $AlCl_3$ in CS_2 yield 6(?)-*chlorocholestanyl acetate*, m. p. 151°, converted by short treatment with KOH–MeOH into 6(?)-*chlorocholestanol*, m. p. 163°, which passes by loss of HCl into cholesterol. Under similar conditions, ergosterol becomes isomerised to a *compound*, $C_{27}H_{42}O$, m. p. 138—140°, $[\alpha]_D^{20}$ −61·1° in $CHCl_3$. αδ-Diphenyl-$\Delta^{\alpha\gamma}$-butadiene, AcCl, and $AlCl_3$ in C_6H_6, but not in CS_2, afford a *compound*, $C_{36}H_{33}O_2Cl$, m. p. 262°, whereas BzCl gives the *substance* $C_{36}H_{30}O$, m. p. 203°. Dicyclopentadiene reacts energetically without giving homogeneous products, whereas distyryl ketone is unexpectedly passive. The base, m. p. 121°, obtained by the action of HCl and HCN on cyclohexene in presence of $AlCl_3$ (cf. A., 1930, 464) does not give an Ac derivative or a nitrosoamine, is stable towards 2N-HCl at 180° and towards KOH–EtOH. Since it is converted smoothly by distillation with soda-lime into cyclohexylamine, the constitution $C_6H_4 {<}^{N(CH \vdots N \cdot C_6H_{11}) \cdot CH \cdot OH}_{CH(OH) \underline{\quad} N \cdot C_6H_{11}}$ is suggested. Dur-

ing the action a *substance*, $C_{25}H_{36}O$, m. p. 150°, is produced. H. WREN.

Photochemical activation of ergosterol. CASTILLE and RUPPOL (Bull. Acad. Roy. Méd. Belg., 1929, 799—821; Chem. Zentr., 1931, i, 3129).— Since the spectrum of ergosterol in hexane shows between 2600 and 3000 Å. four closely neighbouring bands, the three double linkings are considered to belong to one C_6H_6 ring; moreover, the secondary alcoholic group is immediately adjacent to the C_6H_6 ring. Changes caused by irradiation of ergosterol in various solvents were followed in air and in N_2, unchanged ergosterol being determined as digitonide, and unsaturation by Hübl's I method. In absence of O_2 isomerisation occurs. A. A. ELDRIDGE.

Constitution of irradiated ergosterol. A. CASTILLE (Bull. Acad. Roy. Méd. Belg., 1930, 319—325; Chem. Zentr., 1931, i, 3130).—The pairs *iso*ergosterol B and ergosterol B, and *iso*dihydroergosterol A and dihydroergosterol A show in the absorption spectra the differences characteristic of *cis–trans*-isomerism. *cis–trans*-Isomerism as between ergosterol and vitamin-D is postulated.
A. A. ELDRIDGE.

Ergosterol and certain derivatives. DE BOE (Bull. Acad. Roy. Méd. Belg., 1930, 336—375; Chem. Zentr., 1931, i, 3128—3129).—Fractional crystallisation of Reindel's *iso*ergosterol affords iso*ergosterol* B, m. p. 135—136°, α −66° (Ac derivative, m. p. 112°), giving in $CHCl_3$ a yellow colour with H_2SO_4 but no colour with $SbCl_3$ in $CHCl_3$ or $CCl_3 \cdot CO_2H$; Liebermann test blue, becoming green and then brown; and ergosterol B, m. p. 145—146° (Ac derivative, m. p. 139°, affording the *iso*ergosterol B on saponification), yielding *iso*ergosterol B in air. The ultraviolet absorption spectra of the isomerides were studied. Benzoylergosterol has m. p. 164—165° when prepared from BzCl in pyridine at 0°; BzCl at 170° affords a Bz derivative, m. p. 125—126°, which on hydrolysis gives a mixture of ergosterol B and *iso*ergosterol B, from which it may be prepared. Windaus' ergosterol C is a mixture of *iso*ergosterol B and ergosterol B; ergosterol is named ergosterol A. Reduction of ergosterol A with Na and amyl alcohol afforded iso*dihydroergosterol* A, $C_{27}H_{44}O$, m. p. 173—174°, and dihydroergosterol A, $C_{27}H_{44}O$ m. p. 208—209°, the latter (the principal product) containing only one OH group. When similarly treated, ergosterol B is partly isomerised to α-*iso*ergosterol B, m. p. 188—190° (Ac derivative, m. p. 112°, affording on hydrolysis *iso*ergosterol B). Dihydroergosterol A could not be isomerised with HCl (cf. Heilbron and Spring, A., 1930, 210).
A. A. ELDRIDGE.

Refraction of solutions of compounds with many acetylenic linkings. V. KRESTINSKI and N. PERSSIANZEVA (Ber., 1931, **64**, [B], 2363—2370).— Determination of n of αε-diphenyl-γ-methyl-$\Delta^{\alpha\delta}$-pentadi-inen-γ-ol, αε-diphenyl-γ-phenylacetylenyl-$\Delta^{\alpha\delta}$-pentadi-inen-γ-ol, αθ-diphenyl-γζ-dimethyl-$\Delta^{\alpha\eta}$-octadi-inene-γζ-diol, and αθ-diphenyl-γζ-diphenylacetylenyl-$\Delta^{\alpha\eta}$-octadi-inene-γζ-diol in AcOEt, cyclohexanone, amyl alcohol, MeOH, C_6H_6, $COMe_2$, and NH_2Ph leads to the following conclusions. In all cases the observed

vals. of M are considerably greater than the calc., the differences increasing with increasing no. of CPh:C groups. The EM vals., which depend solely on the CPh:C groups, vary considerably from solvent to solvent in the limits, e.g., for the D line from 2·25 in NH_2Ph to 4·00 in $COMe_2$. If the mean vals. for all experiments and solvents are chosen, the data EM_α 3·07, EM_D 3·29, EM_β 3·77, and EM_γ 4·30 may be adopted as mean val. of the increment for the CPh:C group. The influence of the solvent is very great, the compounds differing in this respect from the acetylenic and saturated γ-glycols; the lowest results are observed in NH_2Ph, the highest in $COMe_2$. Much smaller differences are observed with phenylacetylene. $\alpha\varepsilon$-Diphenyl-γ-methyl-$\Delta^{\alpha\delta}$-pentadi-inen-γ-ol, m. p. 110—111°, from AcOEt and Mg phenylacetylenyl bromide, $\alpha\varepsilon$-diphenyl-ψ-phenylacetylenyl-$\Delta^{\alpha\delta}$-pentadi-inen-γ-ol, m. p. 130°, from $CO(OEt)_2$, stereoisomeric $\alpha\delta$-diphenyl-$\gamma\zeta$-dimethyl-$\Delta^{\alpha\eta}$-octadi-inene-$\gamma\zeta$-diols, m. p. 105—106° and 92—96°, respectively, from acetonylacetone and Mg phenylacetylenyl bromide, and $\alpha\theta$-diphenyl-$\gamma\zeta$-diphenylacetylenyl-$\Delta^{\alpha\eta}$-octadi-inene-$\gamma\zeta$-diol, m. p. 136°, from Mg phenylacetylenyl bromide and Et succinate, are described. H. WREN.

Structure and optical rotation. I. Configurational relationship of disubstituted propionic acids containing a phenyl group. II. Optically active trisubstituted methanes containing a phenyl group. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1931, **93**, 749—774).—The method previously used for correlation of the configurations of acids of the type $CHPhAlk \cdot CO_2H$ (I) is applied to the series $CHPhAlk \cdot CH_2 \cdot CO_2H$ (II). Configuratively related members of (I) (this vol., 711, 821) rotate oppositely to the corresponding members of (II). The members of the configuratively related pairs of acids [(I), Alk=Me and Et] and [(II), Alk=Me and Et] themselves rotate in opposite directions, indicating that the $\cdot CO_2H$ and $\cdot CH_2 \cdot CO_2H$ groups are heavier than Me or Et, but lighter than Pr; the same conclusion is reached for the $\cdot [CH_2]_3 \cdot CO_2H$ group. Rearrangement of the relative positions of the heavier and lighter alkyl groups in $CHPhAlkAlk'$ also leads to a change in rotation. The effect of a polar group or of a group absorbing in the near ultra-violet differs with its distance from the asymmetric C atom. The Et ester, b. p. 111°/4 mm., $[\alpha]_D^{25}$ −7·41°, of l-β-phenylbutyric acid, b. p. 134°/4 mm., $[\alpha]_D^{26}$ −12·38° (from the dl-acid by resolution with quinine), is reduced by Na and EtOH in xylene to l-γ-phenylbutyl alcohol, b. p. 117°/8 mm., $[\alpha]_D^{25}$ −9·15°, which with PBr_3 gives l-γ-phenylbutyl bromide, b. p. 120°/17 mm., $[\alpha]_D^{25}$ −18·52°. The Grignard reagent from this is decomposed by ice and dil. HCl to l-β-phenylbutane, b. p. 68°/20 mm., $[\alpha]_D^{24}$ −6·82°. The Et ester, b. p. 110°/2 mm., $[\alpha]_D^{25}$ −7·41°, of l-β-phenylvaleric acid, b. p. 140°/4 mm., $[\alpha]_D^{25}$ −16·5° in C_6H_6, is similarly converted into l-γ-phenylamyl alcohol, b. p. 108°/1 mm., $[\alpha]_D^{25}$ −4·53° (bromide, b. p. 127°/15 mm., $[\alpha]_D^{25}$ −22·23°). The alcohol from Mg l-γ-phenylamyl bromide and paraformaldehyde is converted by PBr_3 into the bromide; the Grignard reagent from this is decomposed by ice to d-γ-phenylhexane (III), b. p. 103°/25 mm., $[\alpha]_D^{24}$ +0·57°. The Et ester, b. p. 123°/2 mm., $[\alpha]_D^{25}$

+3·45°, of d-β-phenylhexoic acid, b. p. 152°/4 mm., $[\alpha]_D^{25}$ +5·93°, is reduced to d-γ-phenylhexyl alcohol, b. p. 127°/5 mm., $[\alpha]_D^{25}$ +2·51° (bromide, b. p. 112°/2 mm., $[\alpha]_D^{25}$ +10·96°, convertible into (III)]. β-Phenylbutylamine, $[\alpha]_D^{24}$ −3·26°, is treated with NOCl in Et_2O at −50° and the resultant chloride converted into a Grignard reagent; decomp. of this with CO_2 and H_2O gives d-β-phenylvaleric acid, b. p. 142°/5 mm., $[\alpha]_D^{25}$ +2·86° in C_6H_6, and l-β-phenylbutane, $[\alpha]_D^{24}$ −1·92° (cf. above), respectively. d-β-Phenylbutyric acid, b. p. 135°/4 mm., $[\alpha]_D^{26}$ +0·96°, is similarly prepared from β-phenylpropylamine, $[\alpha]_D^{24}$ +9·86°. d-δ-Phenylheptoic acid, b. p. 162°/1 mm., $[\alpha]_D^{25}$ +2·12° (prepared from γ-phenylamyl bromide, $[\alpha]_D^{25}$ +11·05°, by the malonate method) (Et ester, b. p. 147°/1 mm., $[\alpha]_D^{25}$ +1·05°); d-ε-phenylheptyl alcohol, b. p. 145°/1 mm., $[\alpha]_D^{25}$ +1·47° (bromide, b. p. 131°/1 mm., $[\alpha]_D^{25}$ +2·45°); d-γ-phenylheptane, b. p. 105°/16 mm., $[\alpha]_D^{25}$ +0·97°; l-δ-phenyloctoic acid, b. p. 170°/1 mm., $[\alpha]_D^{25}$ −0·82° (from γ-phenylhexyl bromide, $[\alpha]_D^{25}$ −11·85°) (Et ester, b. p. 152°/1 mm., $[\alpha]_D^{25}$ −0·49°); l-ε-phenyloctyl alcohol, b. p. 147°/1 mm., $[\alpha]_D^{25}$ −1·1° (bromide, b. p. 146°/1 mm., $[\alpha]_D^{25}$ −2·18°); d-δ-phenyloctane, b. p. 119°/18 mm., $[\alpha]_D^{25}$ +0·62°; d-δ-phenylhexoic acid, b. p. 156°/1 mm., $[\alpha]_D^{25}$ +2·01° (from γ-phenylbutyl bromide, $[\alpha]_D^{25}$ +6·03°) (Et ester, b. p. 145°/1 mm., $[\alpha]_D^{25}$ +1·4°); d-ε-phenylhexyl alcohol, b. p. 127°/1 mm., $[\alpha]_D^{25}$ +1·96° (bromide, b. p. 133°/1 mm., $[\alpha]_D^{25}$ +2·03°), and d-β-phenylhexane, b. p. 100°/22 mm., $[\alpha]_D^{25}$ +1·96°, are described. β-Phenylhexoic acid, $[\alpha]_D^{25}$ −2·32°, is converted by the Hofmann method into l-β-phenylamylamine, b. p. 90°/3 mm., $[\alpha]_D^{25}$ −0·5° in 75% EtOH. H. BURTON.

Conjugated double linkings. XX. Perkin's synthesis. R. KUHN and S. ISHIKAWA (Ber., 1931, **64**, [B], 2347—2352).—Condensation does not occur between PhCHO, crotonic anhydride, and K crotonate or between crotonic acid, Ac_2O, and PbO, whereas in presence of tert. bases, particularly NEt_3, PhCHO and crotonic anhydride afford α-vinylcinnamic [α-benzylidene-Δ^β-butenoic] acid, m. p. 92° (corr.) [dibromide, m. p. 172° (corr.)], oxidised by $KMnO_4$ to BzOH and by CrO_3 to CO_2 and H_2O; it is hydrogenated in presence of Pd–$BaSO_4$ to α-benzyl-n-butyric acid [anilide, m. p. 89° (corr.)]. The corresponding ozonide is converted by boiling H_2O into PhCHO, CH_2O, and $H_2C_2O_4$. p-Nitrobenzaldehyde, crotonic anhydride, and NEt_3 at 100° give α-p-nitrobenzylidene-Δ^β-butenoic acid, m. p. 151·2° (corr.), and α-o-chlorobenzylidene-Δ^β-butenoic acid, m. p. 124·2° (corr.), is derived similarly from o-chlorobenzaldehyde. The mixed enolic anhydride,

$$CHMe:CH \cdot CO \cdot O \cdot C(OH):CH \cdot CH:CH_2,$$

is probably formed intermediately. H. WREN.

Isomerism of 9-fluorene derivatives. A. KLIEGL (Ber., 1931, **64**, [B], 2420—2423; cf. A., 1930, 918, 1031).—Mainly a reply to Bergmann (A., 1930, 1031). Re-examination of the β-fluorene-9-carboxylic acid of Schlenk and Bergmann established its identity with the purified, technical α-acid. 9-Methoxyfluorene-9-carboxylic acid has m. p. about 184° (vigorous decomp.) whether prepared from Na 9-methoxyfluorene and CO_2 or from diphenyleneacetic acid. The 9-benzhydrylfluorene obtained from $CHPh_2Na$ and

9-chlorofluorene has m. p. 217° when crystallised from Pr^{a}OH and subsequently from dioxan. The "isomeride" of m. p. 187—189° is a mol. compound of 9-benzhydrylfluorene and difluorenyl, prepared from its components in Pr^{a}OH. The existence of dimorphous forms of diphenyldiphenylene-ethylene is admitted, but the product considered by Schlenk and Bergmann to be a stereoisomeride is a mixture of the ethylene and ethylene oxide.   H. WREN.

Action of oxalyl chloride on fluorene-9-carboxylic acid. R. STOLLÉ and L. ESTER (J. pr. Chem., 1931, [ii], **132**, 1—14).—Interaction of fluorene-9-carboxylic acid with (COCl)$_2$ in complete absence of H$_2$O gives a very small yield of a cyclic *diphenylenyloxalacetic anhydride*, m. p. 311° (decomp.), to which the structure $(C_6H_4)_2C<^{CO·O}_{CO·CO}$ is assigned on account of its reaction with pyridine to form 1 : 3 : 4-*triketo-2 : 5-bisdiphenylenylcyclopentane* (I), m. p. about 345°, CO (2 mols.), and CO$_2$; (I) is also obtained by interaction of fluorene-9-carboxylic acid, (COCl)$_2$, and pyridine, being then occasionally accompanied by a yellow *substance*, C$_{28}$H$_{16}$O$_3$, m. p. 283°, probably $(C_6H_4)_2C<^{CO·CO}_{O—C(C_6H_4)_2}$. Decomp. of (I) with warm 10% aq. NaOH gives fluorene-9-carboxylic acid, fluorene-9-glyoxylic acid, and decomp. products; with NH$_2$Ph it gives *fluorene-9-glyoxylanilideanil*, m. p. 245°, and with NHPh·NH$_2$ the corresponding *phenylhydrazidephenylhydrazone*, m. p. 190° (decomp.), and fluorene-9-carboxyphenylhydrazide. *Et* ββ′-*diketo-*αα′-*bisdiphenylenyladipate*, m. p. 213°, prepared in good yield by action of (COCl)$_2$ on Et potassiofluorene-9-carboxylate, could not be cyclised to (I), being hydrolysed to its components readily by alkalis, and with difficulty by acids. Attempts to hydrolyse *Et bisdiphenylenylacetonedicarboxylate*, m. p. 129° (from COCl$_2$ and Et potassiofluorene-9-carboxylate), failed; it is converted by Ac$_2$O and anhyd. NaOAc into 9 : 9-*diacetylfluorene*, m. p. 97°, in 90% yield. 2 : 7-*Dibromofluorene-9-carboxylic acid*, m. p. 240° (decomp.), prepared from MgEtBr and 2 : 7-dibromofluorene, gives with (COCl)$_2$ and pyridine the Br$_4$-derivative of (I). *Et fluorene-9-glyoxylate-anil*, m. p. 138°, is prepared by gently warming an equimol. mixture of NH$_2$Ph and Et fluorene-9-glyoxylate.
H. A. PIGGOTT.

Abietic acid. P. LEVY [with H. TILLMANNS] (Ber., 1931, **64**, [B], 2441—2446).—Details are given for the conversion of abietic acid by HBr and HCl in AcOH into dibromodihydro-, m. p. 175—176°, and dichlorodihydro-abietic acid, m. p. 190—192° (decomp.) when slowly heated, respectively. Treatment of the Br$_2$-acid with KOH in EtOH yields a *monohydroxymonohydroabietic acid*, m. p. indef. 154°, not identical with the acid described by Rau and Simonsen (A., 1925, i, 687). Chlorohydroabietic acid, m. p. 192—195° when rapidly heated, is obtained from the Cl$_2$-acid and AcOH. When heated at 200° the Cl$_2$-acid gives abietic acid, whereas in boiling quinoline it gives a *product*, C$_{20}$H$_{30}$O$_2$, m. p. 187°, [α]$_D^{15}$ −73·17°. Monohydroxymonohydroabietic acid, m. p. 225—227°, is smoothly prepared from the Cl-acid and moist Ag$_2$O. Abietic esters unite with H halides under the

same conditions as the acid; *Me*, m. p. 148°, and *Et*, m. p. 138—140° (decomp.), *dibromodihydroabietate*, *Me*, m. p. 163—164°, and *Et*, m. p. 143—145°, *dichlorodihydroabietate* are described. The Cl$_2$-esters are converted by short treatment with AcOH into *Me*, m. p. 126°, and *Et*, m. p. 82—84°, *monochloromonohydroabietate*, respectively.   H. WREN.

4 - Methylthioldiphenylamine - 2′ - carboxylic acid and its derivatives. P. G. SERGEEV (J. Gen. Chem. Russ., 1931, **1**, 279—288).—4-*Methylthioldiphenylamine-2′-carboxylic acid*, m. p. 195—196°, is obtained by the action of 1-bromo-4-methylthiolbenzene on anthranilic acid, and of *p*-methylthiolaniline on *o*-chlorobenzoic acid. The following derivatives were prepared : *Ba* salt, 4-*methylthioldiphenylamine*, m. p. 84·5°; 3-*methylthiolacridone*, m. p. 260—261°; 4-*bromophenylmethylsulphoxide*, m. p. 86—87°; 4-*methylsulphoxidodiphenylamine-2′-carboxylic acid*, m. p. 181°; and 4-*methylsulphonyldiphenylamine-2′-carboxylic acid*, m. p. 186—186·5°.
E. B. UVAROV.

Mixed glycerides of salicylic acid. IV. W. HUMNICKI (Rocz. Chem., 1931, **11**, 670—673).—αγ-Dichlorohydrin β-monosalicylate on treatment with Ag$_2$CO$_3$, AgOH, or AgNO$_3$ does not yield glyceryl β-salicylate. Merck's "glycosal" is glyceryl α-salicylate; on chlorination with SO$_2$Cl βγ-dichlorohydrin α-salicylate, m. p. 58°, is obtained.
R. TRUSZKOWSKI.

Action of phenylcarbimide on aromatic hydroxy-acids. W. HUMNICKI (Rocz. Chem., 1931, **11**, 674—677).—*o*-, *m*-, and *p*-Hydroxybenzoic acids do not yield urethanes with PhCNO, the only product of reaction being CO(NHPh)$_2$, even in non-aq. media. The *phenylurethane* of salol, m. p. 111—112°, yields salol and CO(NHPh)$_2$ on dissolution in aq. solvents.
R. TRUSZKOWSKI.

Preparation of *m*-hydroxybenzonitrile. J. B. CULBERTSON, E. L. CARPENTER, and E. K. NIELSEN (Proc. Iowa Acad. Sci., 1930, **37**, 248—249).—The reactions *m*-nitro——→*m*-amino——→*m*-hydroxy-benzaldehyde——→oxime——→nitrile were employed. Sn was removed by means of aq. NH$_3$ from a solution of the residue of an Et$_2$O extract of the hydroxyaldehyde, the aldehyde adsorbed by the ppt. being extracted with EtOH. The aldehyde was purified by crystallisation from CCl$_4$ after treatment with norite. On dehydration of the oxime with Ac$_2$O the Ac derivative is preferably hydrolysed with 10% KOH without previous isolation.   CHEMICAL ABSTRACTS.

Physical properties of optical antipodes. A. N. CAMPBELL (Ber., 1931, **64**, [B], 2476—2477; cf. A., 1930, 1289).—A reply to Kortüm (this vol., 956).
H. WREN.

Azomethines of homophthalimide and its *n*-aryl derivatives. A. MEYER and R. VITTENET (Compt. rend., 1931, **193**, 531—533).—Homophthalimide when condensed with the NO-derivatives of NPhMe$_2$, NPhEt$_2$, antipyrine, and *p*-tolylantipyrine gives p-*dimethylaminophenyl*-, m. p. 243°, p-*diethylaminophenyl*-, m. p. 196—197°, *antipyryl*-, m. p. 224—225° (decomp.), and p-*tolylantipyryl-iminophthalonimide*, m. p. 227—228°. The N-*Ph*, m. p. 210°, N-p-*tolyl*, m. p. 223—224°, N-α-*naphthyl*, m. p. 239—

240°, and N-β-*naphthyl*, m. p. 180—181° (decomp.), derivatives of antipyryliminophthalonimide are similarly prepared from the corresponding *N*-arylated homophthalimides. A. A. LEVI.

Differing modes of reaction of magnesium phenyl bromide and lithium phenyl towards derivatives of naphthalic acid. G. WITTIG, M. LEO, and W. WIEMER (Ber., 1931, 64, [*B*], 2405—2411).—The action of more than 4 mols. of MgPhBr on Me naphthalate leads to ill-defined mixtures, whereas from naphthalic anhydride 9 : 10-dihydroxy-9 : 10-diphenylacenaphthene, m. p. 155—156° (cf. Beschke, A., 1909, i, 917), is produced, reaction being thus accompanied by reduction. From 1 : 8-dibenzoylnaphthalene and MgPhBr an isomeric 9 : 10-*dihydroxy*-9 : 10-*diphenylacenaphthene*, m. p. 171—173°, is produced. Both glycols are converted by HCl in boiling AcOH into 9 : 9-diphenylacenaphthenone and by HCl in cold CHCl$_3$ into 9 : 10-*dichloro*-9 : 10-*diphenylacenaphthene*, m. p. 185° (decomp.), transformed by Cu powder into 9 : 10-*diphenylacenaphthylene*, m. p. 159·5—161°.

Naphthalic anhydride and 4 mols. of LiPh yield resins, whereas with 2 mols. of the reagent the lactone of 1 - hydroxybenzhydrylnaphthalene - 8 - carboxylic acid, C$_{10}$H$_6$$\langle$CO/CPh$_2$$\rangle$O, m. p. 203—204°, is produced. This adds a further mol. of LiPh, yielding the *compound* C$_{30}$H$_{22}$O$_2$ (I) (? C$_{10}$H$_6$$\langle$CPh(OH)/CPh$_2$$\rangle$O), m. p. 202—203·5°, also obtained from excess of LiPh and Me naphthalate or 1 : 8-dibenzoylnaphthalene. Further reaction to form 1 : 8-di(hydroxybenzhydryl)naphthalene does not take place. (I) is converted by HCl in AcOH into the oxonium *salt*, C$_{10}$H$_6$$\langle$CPhCl/CPh$_2$$\rangle$O,HCl, m. p. 153—155°.

H. WREN.

Rotenone. XV. Structure of derric acid. F. B. LA FORGE (J. Amer. Chem. Soc., 1931, 53, 3896—3901).—Derric acid is now considered to be (I) (cf. A., 1930, 1187) and rissic acid (Takei, this vol., 490) to be (II), since decarboxyrissic acid (III) (Takei,

MeO$\langle$ $\rangle$CH$_2$·CO$_2$H   MeO$\langle$ $\rangle$CO$_2$H
MeO   O·CH$_2$·CO$_2$H   MeO   O·CH$_2$·CO$_2$H
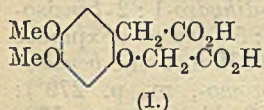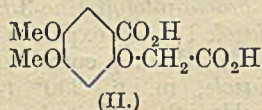
(I.)   (II.)

loc. cit.) [*Br*-derivative, m. p. 150°; *Cl*-derivative, m. p. 146° (*Et* ester, m. p. 83°), from (III) and PCl$_5$; the *NO$_2$*-derivative, m. p. 214—215° (*Et* ester, m. p. 164—165°), is prepared from (II) and HNO$_3$, and is described by Takei as a nitrodimethoxybenzoic acid] is identical with 3 : 4-*dimethoxyphenoxyacetic acid*, m. p. 116—117°, obtained from Na 3 : 4-dimethoxyphenoxide and CH$_2$I·CO$_2$Et in EtOH. Takei's suggestion that (III) is 2 : 5-*dimethoxymandelic acid*, m. p. 101° (softens at 90°), is disproved by synthesis of the latter from 2 : 5-dimethoxybenzaldehyde by the usual method. 2 : 3-*Dimethoxymandelic acid* has m. p. 96°. H. BURTON.

spiro-**Compounds. I.** P. K. PAUL (J. Indian Chem. Soc., 1931, 8, 717—724).—*cyclo*Pentane-, m. p. 257°, *cyclo*hexane- (I), m. p. 266°, 3-*methyl*cyclo-

hexane-, m. p. 259°, and 4-*methyl*cyclohexane-, m. p. 252°, -spiro-2′ : 4′-*dicyanocyclobutane*-2′ : 4′-*dicarboxylimides* are prepared by Kerr's method (A., 1929, 445) from the appropriate Guareschi imide and CH$_2$I$_2$. Hydrolysis of (I) with 2% NaOH gives *cyclo*hexanespiro-2′ : 4′-*dicarbamylcyclobutane*-2′ : 4′-*dicarboxylic acid*, m. p. 180° (decomp.), whilst hydrolysis of the other imides with 10% KOH affords *cyclo*pentane-, m. p. 188°, 3-*methyl*cyclohexane-, m. p. 211°, and 4-*methyl*cyclohexane-, m. p. 204°, -spiro-2′ : 4′-*dicyano*-2′-*carbamyl*cyclobutane-4′-*carboxylic acids*. These products are hydrolysed further by 20% NaOH to *cyclo*pentane-, m. p. 190° (decomp.), *cyclo*hexane-, m. p. 190° (decomp.), 3-*methyl*cyclohexane-, m. p. 173° (decomp.), and 4-*methyl*cyclohexane-, m. p. 162° (decomp.), -spirocyclobutane-2′ : 2′ : 4′ : 4′-*tetracarboxylic acids*, which when heated at 5° above their m. p. give mixtures (*cis* and *trans*) of the corresponding 2′ : 4′-dicarboxylic acids, separable by treatment with AcCl (whereby the *cis*-form· is removed as its anhydride). trans-*cyclo*Hexane-, m. p. 178°, and trans-3-*methyl*cyclohexane-, m. p. 176°, -spirocyclobutane-2′ : 4′-*dicarboxylic acids*, and cis-*cyclo*hexane-, m. p. 159—162°, and cis-4-*methyl*cyclohexane-, m. p. 180°, -spirocyclobutane-2′ : 4′-*dicarboxylic anhydrides* are described. The above compounds resemble in stability to alkalis the corresponding derivatives of norpinic acid described by Kerr (*loc. cit.*). H. BURTON.

Constituents of petroleum. I. J. VON BRAUN and others.—See this vol., 1396.

Autoxidation of benzaldehyde. E. RAYMOND.—See this vol., 1375.

Attempted isolation of copper benzaldehyde. D. B. BRIGGS, H. SAENGER, and W. WARDLAW (J.C.S., 1931, 2552—2555).—The substance obtained by Bernouilli and Schaaf (A., 1922, i, 1029) by the action of Cu on PhCHO in PhMe is not Cu benzaldehyde, but *benzaldehyde Cu benzoate*, Cu(OBz)$_2$,PhCHO,H$_2$O (I). When crystallised from pyridine *dipyridine Cu benzoate*, Cu(OBz)$_2$,2C$_5$H$_5$N,H$_2$O, results, formulated 2[Cu(PhCHO)$_2$],5C$_5$H$_5$N by Schaaf (A., 1923, i, 799); when heated this compound loses 1 mol. of H$_2$O and 1 mol. of pyridine to give *monopyridine Cu benzoate*, Cu(OBz)$_2$,C$_5$H$_5$N. On prolonged heating Cu(OBz)$_2$ is left and on keeping with quinoline, C$_5$H$_5$N is replaced to give *monoquinoline Cu benzoate*. Cu(OBz)$_2$ when heated with PhCHO in PhMe produces (I). It is suggested that BzO$_2$H is formed as an intermediary. F. R. SHAW.

Condensation of aldehydes and ketones with ethyl chloroacetate. II. Aromatic aldehydes and ketones. B. N. RUTOVSKI and N. A. DAEV (J. Gen. Chem. Russ., 1931, 1, 185—189).—Action of the Na compound of PhCHO on Et chloroacetate gives CH$_2$Ph·OH, CH$_2$Ph·CHO, and NaCl. The Na compound of COPh$_2$ gives CHPh$_2$·OH, diphenylglycidic acid, and NaCl. The presence of electronegative Cl in the α position renders the H atom in the CH$_2$Cl group mobile, the reaction proceeding :

2CAr$_2$·ONa + CH$_2$Cl·CO$_2$Et $\longrightarrow$ 2CHAr$_2$·ONa $\longrightarrow$

CHAr$_2$·OH + CAr$_2$$\langle$O/CH·CO$_2$Et· E. B. UVAROV.

Action of phenylcarbimide on some aromatic amino-oximes. C. V. GHEORGHIU (Bull. Soc. chim., 1931, [iv], **49**, 1205—1210).—In contrast to the thiocarbimides (this vol., 210), phenylcarbimides yield products with amino-oximes, formed by addition of 2 mols. of PhNCO to 1 mol. of amino-oxime. Thus *p*-aminobenzaldoxime in C_6H_6 yields *dicarbanilido-p-aminobenzaldoxime*, $NHPh \cdot CO \cdot NH \cdot C_6H_4 \cdot CH:NO \cdot CO \cdot NHPh$, m. p. 176—177° (decomp.); *dicarbanilido-m-aminobenzaldoxime*, m. p. 171° (decomp.), and -*p-aminoacetophenoneoxime*, m. p. 178—179° (decomp.), are similarly obtained in $COMe_2$, and *dicarbanilido-m-aminoanisaldoxime*, m. p. 170—171° (decomp.), and -*acetophenoneoxime*, m. p. 175—176°, in Et_2O. The dicarbanilido-*o*-aminobenzaldoxime, m. p. 195—196° (decomp.), obtained from *o*-aminobenzaldoxime in Et_2O is probably β-2-keto-3-phenyl-1 : 2 : 3 : 4-tetrahydro - 4 - quinazolylhydroxylaminecarbanilide, a structure which is supported by the fluorescence of its solution in H_2SO_4 on dilution with H_2O.
　　　　　　　　　　　　　　　　R. BRIGHTMAN.

Condensation of aldehydes with hydrazones. V. Condensation of benzaldehyde with the phenylhydrazones of anis- and *p*-dimethylaminobenz-aldehydes. A. GIACALONE (Gazzetta, 1931, **61**, 639—642).—PhCHO condenses with anisaldehydephenylhydrazone, giving 4 : 4'-*di-p-methoxybenzylidenehydrazinotriphenylmethane*, m. p. 166—167°, and with *p*-dimethylaminobenzaldehyde giving 4 : 4' - *di - p - dimethylaminobenzylidenehydrazinotriphenylmethane*, m. p. 213—214°, the product in each case being identical with that obtained from the aldehyde $R \cdot C_6H_4 \cdot CHO$ and dihydrazinotriphenylmethane. Vanillin condenses with dihydrazinotriphenylmethane giving 4 : 4'-*di-p-hydroxy-m-methoxybenzylidenehydrazinotriphenylmethane* m. p. 154°, but vanillinphenylhydrazone does not condense with PhCHO.
　　　　　　　　　　　　　　E. E. J. MARLER.

Behaviour of phenylhydrazones with condensing media. A. GIACALONE [with A. DOMENICO] (Gazzetta, 1931, **61**, 642—645).—When benzaldehydephenylhydrazone is heated with $ZnCl_2$ or dissolved in H_2SO_4, dibenzylidenedihydrazinotriphenylmethane and a salt of $NHPh \cdot NH_2$ are formed, on account of partial hydrolysis of the hydrazone, the liberated PhCHO condensing with the remaining hydrazone. The phenylhydrazones of anisaldehyde and salicylaldehyde react similarly with $ZnCl_2$, but salicylaldehyde does not react with H_2SO_4, and anisaldehyde reacts only in presence of Et orthoformate.
　　　　　　　　　　　　　　E. E. J. MARLER.

Action of bromine on *o*-tolylhydrazones and *o*-nitrophenylhydrazones. F. D. CHATTAWAY and A. B. ADAMSON (J.C.S., 1931, 2787—2792).—The action of 2 mols. of Br on the *o*-tolylhydrazones of *o*-, *m*-, and *p*-nitrobenzaldehydes results in bromination in the ω-position and in the 3-position in the *o*-tolyl nucleus; excess of Br causes further substitution in the 5-position, and less Br gives mixtures of Br_2-derivative and unchanged hydrazone. The products described are : ω-*bromo*-m-*nitrobenzaldehyde*-3-*bromo*-, m. p. 164°, -3 : 5-*dibromo*-, m. p. 152°, ω-*bromo*-p-*nitrobenzaldehyde*-3-*bromo*-, m. p. 186°, and -3 : 5-*dibromo*-o-*tolylhydrazone*, m. p. 175°. These

react with NH_3 to give respectively : 3-*bromo*-, m. p. 149°, 3 : 5-*dibromo*-o-*tolyl*-m-, m. p. 150°, 3-*bromo*-, m. p. 152°, and 3 : 5-*dibromo*-o-*tolyl*-p-*nitrobenzylhydrazidine*, m. p. 171°, and with NaOAc, m-*nitrobenz*-β-*acetyl*-3 : 5-*dibromo*-, m. p. 176°, and p-*nitrobenz*-β-*acetyl*-3-*bromo*-o-*tolylhydrazide*, m. p. 195°, are obtained. ω - *Bromo* - o - *nitrobenzaldehyde* - 3 - *bromo* - o - *tolylhydrazone*, m. p. 106° (3 : 5-*dibromo*-, m. p. 137°), is converted by NH_3 into 3-*keto*-1 : 2-endo-3'-*bromo*-o-*tolylimino* - 2 : 3 - *dihydro* - 1 : 2 - *benzisodiazole* 1-*oxide*, explodes 151° (3 : 5-*dibromo*-, explodes 145°), which is reduced to the corresponding *benzisodiazole*, m. p. 181°.

The compounds obtained from the nitrophenylhydrazones of PhCHO and nitrobenzaldehydes behave similarly : ω-*bromobenzaldehyde*-, m. p. 166°, ω-*bromo*-m-*nitrobenzaldehyde*-, m. p. 201°, and ω-*bromo*-p-*nitrobenzaldehyde*-4-*bromo*-2-*nitrophenylhydrazone*, m. p. 242°; 4-*bromo*-2-*nitrophenyl*-, m. p. 188°, 4-*bromo*-2-*nitrophenyl*-m-*nitro*-, m. p. 245° (decomp.) [*hydrochloride*, m. p. 235° (decomp.)], and 4-*bromo*-2-*nitrophenyl* - p - *nitro-benzenylhydrazidine*, m. p. 249°; m-*nitrobenz* - β - *acetyl*-4 -*bromo* - 2 - *nitrophenylhydrazide*, m. p. 173°; ω-*bromo*-o-*nitrobenzaldehyde* 2-*nitrophenylhydrazone*, m. p. 137°, and 3-*keto*-1 : 2-endo-4'-*bromo*-2'-*nitrophenylimino* - 2 : 3 - *dihydro*-1 : 2 - *benzisodiazole* 1-*oxide*, explodes at 142°.
　　　　　　　　　　　　　　F. R. SHAW.

Action of bromine and of chlorine on 2 : 4-dinitrobenzaldehyde-phenyl- and -*p*-tolyl-hydrazones. F. D. CHATTAWAY and A. B. ADAMSON (J.C.S., 1931, 2792—2796).—Both Cl and Br substitute in the *o*- and *p*-positions in the Ph residue and in the *o*- and ω-positions in the *p*-tolyl residue of the hydrazones, chlorination proceeding further than bromination. The following are described : ω-*bromo*-2 : 4-*dinitrobenzaldehyde*-4-*bromo*-, m. p. 176° (decomp.), and -2 : 4-*dibromo*-, m. p. 202° (decomp.), ω-*chloro*-2 : 4-*dinitrobenzaldehyde*-2 : 4-*dichloro*-, m. p. 196° (decomp.), and -2 : 4 : 6-*trichloro-phenylhydrazone*, m. p. 129° (decompose when treated with NH_3 or NaOAc); ω-*bromo*-2 : 4-*nitrobenzaldehyde*-3-*bromo*-p-*tolylhydrazone*, m. p. 141° (-3 : 5-*dibromo*-, m. p. 152°), treated with NH_3 affords 6-*nitro*-1 : 2-endo-3'-*bromo*-p-*tolylimino*-3-*keto*-2 : 3-*dihydro*-1 : 2-*benzisodiazole* 1-*oxide*, explodes 133° (-3 : 5-*dibromo*-, explodes 142°), which is converted by EtOH into the *benzisodiazole*, m. p. 250° (-3 : 5-*dibromo*-, m. p. 279°); ω-*chloro*-2 : 4-*dinitrobenzaldehyde*-3-*chloro*-, m. p. 170° (decomp.), and -3 : 5-*dichloro*-p-*tolylhydrazone*, m. p. 151° (decomp.); 2 : 4-*dinitrobenzaldehyde*-2 : 4-*dibromo*-, m. p. 204°, and -2 : 4-*dichlorophenylhydrazone*, m. p. 207°, -3-*bromo*-, m. p. 179°, -3 : 5-*dibromo*-, m. p. 182°, -3-*chloro*-, m. p. 192°, and -3 : 5-*dichloro*-p-*tolylhydrazone*, m. p. 200°.
　　　　　　　　　　　　　　F. R. SHAW.

Colours produced by alcoholic alkali hydroxides and concentrated sulphuric acid on certain chloro- and bromo-nitro-3-hydroxybenzaldehyde-*p*-nitrophenylhydrazones. An electronic explanation. H. H. HODGSON and E. W. SMITH (J.S.C.I., 1931, **50**, 358—360T).—6-Chloro-2 : 4-dinitro - 3 - hydroxybenzaldehyde - p - nitrophenylhydrazone develops a vivid royal-blue colour on treatment with aq. NaOH, whereas 2-chloro-4 : 6-dinitro-3-hydroxybenzaldehyde-*p*-nitrophenylhydrazone gives only

a claret colour on warming, a behaviour which recalls that of 2 : 5-dichloro-6-nitrobenzaldehydephenylhydrazone, the only exception to Chattaway and Clemo's generalisation (J.C.S., 1923, **123**, 3043). The anomalous behaviour cited is connected with the presence of a Cl atom in position 2. An explanation of the variations of colour encountered, and also of the colours produced by conc. H_2SO_4 on the Br-products in terms of modern electronic theory is advanced, the variations depending on the extent of ionisation of the imino-H.

Production of phenylglyoxal. C. NEUBERG and E. HOFMANN (Biochem. Z., 1931, **239**, 495—497).— The method previously described (this vol., 486) is cheaper and better than that of Henze (this vol., 843). If desired the nitrosylsulphuric acid may be replaced by H_2SO_4 and $NaNO_2$. The yield is then 35—37%. *p*-Tolylglyoxal can be obtained in the same way from *p*-methylacetophenone. W. McCARTNEY.

Condensation of aromatic aldehydes with nitromethane in presence of alcoholic sodium hydroxide. N. A. LANGE and W. E. HAMBOURGER (J. Amer. Chem. Soc., 1931, **53**, 3865—3867).— Gradual addition of alcoholic NaOH to vanillin benzyl ether and $MeNO_2$ in EtOH below 15°, and subsequent acidification, gives a 97% yield of ω-nitro-4-benzyloxy-3-methoxystyrene, which could not be prepared by Kobayashi's method (A., 1928, 169). ω-Nitro-3 : 4-methylenedioxystyrene, m. p. 161·5° (corr.), is prepared similarly from piperonal in 74% yield. H. BURTON.

Synthesis of alkyl*cyclo*pentanones. J. VON BRAUN, W. KELLER, and K. WEISSBACH (Annalen, 1931, **490**, 179—188).—Alkylsuccinic acids, prepared from the appropriate cyanohydrin and Et sodiocyanoacetate (cf. Higson and Thorpe, J.C.S., 1906, **89**, 1465), are converted into Et esters, which are reduced to glycols (Na–EtOH); these are converted successively into the corresponding dibromides, dicyanides, and adipic acids, which are finally distilled with $FeSO_4$, or, alternatively, the dibromides are treated with Mg and CO_2. The following are described : *Et αβ-dicyano-n-hexoate*, b. p. 173—177°/12 mm.; *β-propyl-adiponitrile*, b. p. 174—176°/12 mm., and *-adipic acid*, m. p. 45—49°, b. p. 184—186°/0·1 mm.; *3-n-propyl*cyclopentanone, b. p. 190—191° (*oxime*, m. p. 121—122°; *semicarbazone*, m. p. 178—179°; *p-nitrobenzylidene* derivative, m. p. 222°); *Et αβ-dicyano-α-ethyl-n-butyrate*, b. p. 160—162°/13 mm.; *Et α-methyl-α′-ethylsuccinate*, b. p. 120°/13 mm.; *βγ-di-(hydroxymethyl)-n-pentane*, b. p. 141—143°/14 mm. (*dibromide*, b. p. 114—116°/13 mm.); *β-methyl-β′-ethyladipic acid*, m. p. 58—70°, b. p. 176—178°/0·7 mm. (probably a mixture of stereoisomerides) (*dinitrile*, b. p. 164—166°/13 mm.); *3-methyl-4-ethyl*cyclopentanone, b. p. 180° (*oxime*, b. p. 117—118°/11 mm.; *semicarbazone*, m. p. 208—209°; *bis-p-nitrobenzylidene* derivative, m. p. 192°); *Et H*, b. p. 154—156°/12 mm., and *Et₂*, b. p. 120—122°/14 mm., *α-methyl-α-ethylsuccinates*; *γ-methyl-γ-hydroxymethylpentan-α-ol*, b. p. 142—144°/14 mm. (*dibromide*, b. p. 114°/14 mm.); *3-methyl-3-ethyl*cyclopentanone, b. p. 174° (*semicarbazone*, m. p. 170°; p-*nitrobenzylidene* derivative, m. p. 180°); *Et H trimethylsuccinate*, b. p. 158°/14

mm.; *ββγ-trimethylbutan-αδ-diol*, b. p. 134—136°/12 mm. (*dibromide*, b. p. 106°/12 mm.). From the last-named dibromide by action of KCN and subsequent hydrolysis is formed a small amount of *δ-bromo-βγγ-trimethyl-n-valeric acid*, b. p. 114—116°/0·3 mm. (*Et* ester, b. p. 122°/12 mm.), in which the Br is not replaceable by Mg or org. bases. No definite ketonic product was isolated by action of Mg and CO_2 on the dibromide. Reduction of *iso*camphorphorone with Pd–H_2 gives 3 : 3 : 4-*trimethyl*cyclo*hexanone*, b. p. 184—188° (*oxime*, m. p. 100°; *semicarbazone*, m. p. 177°; *di-p-nitrobenzylidene* derivative, m. p. 226°), from which no recognisable products were obtained by oxidation with dil. aq. $KMnO_4$ at 3—4°.
H. A. PIGGOTT.

Orientation phenomena among the *cyclo*hexanones. I. R. CORNUBERT. **II.** R. CORNUBERT and R. HUMEAU. **III.** R. CORNUBERT and A. MAUREL. **IV.** R. CORNUBERT, R. HUMEAU, H. LE BIHAN, and A. MAUREL (Bull. Soc. chim., 1931, [iv], **49**, 1229—1238, 1238—1248, 1248—1259, 1260—1266).—I. The formation of the dissymmetric ·CH_2·CO·CRMe· and symmetric ·CHR·CO·CHMe· types of ketone in the alkylation or arylation of ketones ·CH_2·CO·CHMe· is an orientation phenomenon and is not due to transposition. Alkylation of *cyclo*hexanone affords successively (1) 2-alkyl*cyclo*hexanone ; (2) a mixture of 85—90% of 2 : 2-dialkyl*cyclo*hexanone and 10—15% of 2 : 6-dialkyl derivatives ; (3) 2 : 2 : 6-trialkyl- and (4) 2 : 2 : 6 : 6-tetra-alkyl-*cyclo*hexanone. The secondary and condensation reactions increase with concentration of the ketone and the temp. Similarly, alkylation or arylation of a 2-alkyl- or -aryl-*cyclo*hexanone affords 85—90% of the 2 : 2- and 10—15% of the 2 : 6-derivative, the relative percentages depending on the nature of the halogen atom in the alkyl halide, chlorides yielding more of the 2 : 6-derivative. Benzylation of 2-methyl*cyclo*hexanone affords a mixture of the 2-methyl-2 : 6- and -6 : 6-dibenzyl derivatives. The nature of the 2-alkyl group in the alkyl*cyclo*hexanone has little influence. Attempts at phenylation or *cyclo*hexylation failed. Alkylation of 3-methyl*cyclo*hexanone yields mainly the 3 : 6-, together with a trace of 3 : 6 : 6-derivative ; the 2 : 3-derivative has not been detected. The 3-Me group can thus inhibit the formation of the 2 : 3 : 6-derivative if there is an alkyl group in the 6-position. Alkylation of 2 : 3-dimethyl*cyclo*hexanone affords 77% of the 2 : 2 : 3- and 23% of the 2 : 3 : 6-derivative. Alkylation of 4-methyl*cyclo*hexanone affords successively (1) 4-methyl-2-alkyl*cyclo*hexanone, (2) a mixture of 88% of 2 : 6- and 12% of 2 : 2-dialkyl derivatives, (3) 2 : 2 : 6-trialkyl-4-methyl-, and (4) 2 : 2 : 6 : 6-tetra-alkyl-4-methyl-*cyclo*hexanone, exactly as in the methylation of *cyclo*hexanone itself. The formation of the dissymmetric ketone is attributed to dehydration of the 2-methyl*cyclo*hexanol, ·CH_2·CH(OH)·CHR·, yielding ·CH_2·CH:CHR· and the readier sodiation of the group>CHR than of >CH_2. The results are not interpreted by the theory of steric hindrance and the formation of sodio-derivatives >C·ONa is supported by the exclusive formation of 2 : 2 : 5-trimethyl*cyclo*hexanone by methylation of 2 : 5-dimethyl*cyclo*hexanone, whilst amyl formate and $NaNH_2$ yield the 2 : 5-dimethyl-6-hydroxymethylene derivative.

II. Variable results for the composition of the reaction mixture obtained in the alkylation of 2-methyl-*cyclo*hexanones are attributed partly to viscous products which accompany the cryst. benzylidene compound in amounts decreasing as the difference in b. p. between methyl*cyclo*hexanone and the alkyl derivative increases and with the efficiency with which the methyl*cyclo*hexanone is eliminated with NaHSO$_3$. The viscous products are mixtures of the benzylidene derivatives of 2-methyl*cyclo*hexanone and its alkyl derivatives, the viscous product from 2 : 6-dimethyl-*cyclo*hexanone affording with H$_2$ in presence of Ni and condensation with PhCHO the tetrahydropyrone of 2-methyl-6-benzyl*cyclo*hexanone. The formation of the tetrahydropyrone of 2-methyl*cyclo*hexanone and the reactivity of the latter with NaHSO$_3$, although destroyed on alkylation, limit the accuracy of the method of calculating the composition of the reaction mixture. There is no evidence that impurities in the NaNH$_2$ effect transposition or that transposition occurs on working up or analysis. Me$_2$SO$_4$ yields 88% of 2 : 2- and 12% of 2 : 6-derivatives, MeI affording 89% and 11%, respectively. Benzylation of 2-methyl*cyclo*hexanone with CH$_2$PhBr affords 94% of dissymmetric and 6% of symmetric isomeride, CH$_2$PhCl yielding 89—90% and 11—10%, respectively.

III. Methylation of 3-methyl*cyclo*hexanone by NaNH$_2$ and Me$_2$SO$_4$ affords a series of fractions, b. p. 172—192°, from which have been obtained the oximes of 2 : 5-dimethyl*cyclo*hexanone, pulenone (2 : 2 : 5-trimethyl*cyclo*hexanone), and 2 : 2 : 5 : 6-tetramethyl-*cyclo*hexanone, condensation with PhCHO in presence of HCl affording the benzylidene compound of pulenone and the tetrahydropyrones of 2 : 5-dimethyl- and 2 : 5 : 6-trimethyl-*cyclo*hexanone. The 3-Me group has an almost exclusively *p*-orienting influence and methylation of 2 : 5-dimethyl*cyclo*hexanone affords exclusively pulenone, the 2 : 5 : 6-trimethyl*cyclo*hexanone resulting partly from the formation of a 5 : 5-Na$_2$ derivative in the action of NaNH$_2$ on 3-methyl-, but mainly from the 2 : 3-dimethyl-*cyclo*hexanone which has not been characterised. Allylation of 3-methyl-*cyclo*hexanone similarly affords successively 2-methyl-5-allyl- (with-probably, a little 3-methyl-2-allyl-) and 2-methyl-5 : 5-diallyl-, with possibly traces of 3-methyl-2 : 6-diallyl-*cyclo*hexanone. The 2-methyl-5-propyl*cyclo*hexanone obtained on hydrogenation affords with 2 mols. of PhCHO two isomeric tetrahydropyrones. Methylation of *l*-menthone affords 2 : 5-dimethyl- with possibly traces of 1 : 2-dimethyl-5-*iso*propyl*cyclo*hexanone, which unlike dihydrocamphorone does not give an abnormal benzylidene compound but a tetrahydropyrone in poor yield.

IV. Allylation of *cyclo*hexanone with 2 mols. of NaNH$_2$ and 2 mols. of allyl bromide affords 89% of 2 : 2-diallyl- and 11% of 2 : 6-diallyl-*cyclo*hexanone, allylation of allyl*cyclo*hexanone affording substantially the same mixture (86 : 14). Although the Na derivative of *cyclo*hexanone with allyl*cyclo*hexanone and subsequent treatment with allyl bromide gives three times the normal yield of diallyl*cyclo*hexanone, this observation is insufficient to prove the sodiating action of a Na derivative, and the formation of a benzylallyl*cyclo*hexanone when the allyl*cyclo*hexanone is replaced by benzyl*cyclo*hexanone cannot be attributed to sodiation by the sodio-derivative. The greater reactivity of Na in 2-sodio-2-methyl- than in 2-sodio-6-methyl-*cyclo*hexanone towards alkyl bromides, the reactivity to alkyl chlorides being similar, and the differing sodiating action of the sodiomethyl-alkyl*cyclo*hexanones are further factors in determining the proportions of the alkylated products. Methylation of 2 : 3-dimethyl*cyclo*hexanone affords 77% of 2 : 2 : 3-trimethyl- and 23% of 2 : 3 : 6-trimethyl-*cyclo*hexanone. Benzylation of *cyclo*hexanone affords, in addition to benzyl*cyclo*hexanone, 2 : 2-dibenzyl-*cyclo*hexanone, m. p. 53—54°, with a little benzyl-*cyclo*hexylidene*cyclo*hexanone. 2-Benzyl*cyclo*hexanone gives 98·5—99·5% of 2 : 2-dibenzyl*cyclo*hexanone, with traces of the 2 : 6-dibenzyl derivative, m. p. 103—103·5°.   R. BRIGHTMAN.

Condensation of ketones in the presence of hydrochloric acid under pressure. B. N. DOLGOV and I. N. VOLNOV (J. Gen. Chem. Russ., 1931, **1**, 340—344).—The velocity of condensation and yield are increased considerably by the use of high pressures. The high pressures allow the use of large quantities of HCl necessary for condensation of the higher ketones.   E. B. UVAROV.

ω-Substituted acetophenone derivatives. I. ω-Halogeno-derivatives of *ωm*- and *ωp*-dinitro-acetophenone. J. W. BAKER (J.C.S., 1931, 2416—2426).—Of the ω-halogeno-derivatives of *m*- and *p*-nitroacetophenone only the I-compounds are attacked by AcNO$_3$. The resulting ω-NO$_2$-derivatives are stable only in absence of air and H$_2$O, whilst the ω-bromo-ω-nitro-derivatives, obtained indirectly, are more stable. These results are discussed on the basis of electronic theories. The action of Cl$_2$ on molten *m*-nitroacetophenone gives the ω-Cl-derivative, m. p. 103° (A., 1928, 1009), converted by KBr in EtOH and H$_2$O into the ω-Br-derivative, also obtained by the method of Evans and Brooks (A., 1908, i, 338). This is converted by KI in EtOH into ω-*iodo*-m-*nitroacetophenone*, m. p. 96°, the solution of which in Ac$_2$O and HNO$_3$, when evaporated in vac., gives ω-*iodo*-m*ω*-*dinitroacetophenone*, analysed in a special apparatus, and hydrolysed to *m*-nitrophenylglyoxal (*semicarbazone*, m. p. 203°; osazone, m. p. 233°) (A., 1911, i, 987), *m*-nitrophenacyl acetate (*semicarbazone*, m. p. 177°) (A., 1908, i, 338), *m*-nitrobenzoic acid, and a little *m*-nitrobenzoylformic acid, m. p. 105° (A., 1880, 253), also obtained by oxidation of *m*-nitrophenylglyoxal with HNO$_3$. ω-Bromo-*p*-nitroacetophenone with KI in EtOH gives ω-*iodo*-*p*-*nitroacetophenone*, m. p. 97—98°, converted by Ac$_2$O and HNO$_3$ into (?) ω-iodo-*pω*-dinitroacetophenone, which is hydrolysed by H$_2$O to (?) p-*nitrophenacyl acetate*, m. p. 124°, converted by NHPh·NH$_2$ in H$_2$O into the *phenylhydrazone*, m. p. 178°, of *p*-nitrophenacyl alcohol, and oxidised by HNO$_3$ to p-*nitrobenzoylformic acid*, m. p. 150° (previous softening). The *K* salt of ω*p*-dinitroacetophenone (A., 1903, i, 16) with Br in H$_2$O gives *p*-nitrobenzoic acid, whilst in anhyd. Et$_2$O it gives ω-*bromo*-ω*p*-*dinitroacetophenone*, m. p. 89—90°, converted by H$_2$O or KI into *p*-nitrobenzoic acid. *m*ω-Dinitrostyrene with Br in hot CHCl$_3$ gives αβ-*dibromo*-α-*nitro*-β-m-*nitrophenylethane*,

m. p. 158°, converted by NaOAc in EtOH into ω-bromo-mω-dinitrostyrene, m. p. 114—115°. This with KOH in MeOH gives a small amount of α-bromo-α-nitro-β-methoxy-β-m-nitrophenylethane, m. p. 103—104°, and the Me_2 acetal of mα-dinitroacetophenone, which is hydrolysed to the ketone. The K salt of this with Br in anhyd. Et_2O gives ω-bromo-mω-dinitroacetophenone, m. p. 87°, converted by H_2O or KI into m-nitrobenzoic acid. A. A. Levi.

Reactivities of ω-halogen atoms in acetophenone. D. Matheson and J. E. Humphries (J.C.S., 1931, 2514—2516).—The reactivities of Cl, Br, and I in the ω-position in COPhMe towards NH_2Ph in EtOH at 40° are in the order I>Br>Cl, the reaction being followed by the titration of the halogen acid liberated. The Cl-compound shows reactivity only when NH_2Ph is in excess.

F. R. Shaw.

Ester-ester-enol isomerisation and the dimeric diphenylthioketen. A. Schönberg, L. von Vargha, and H. Kaltschmitt (Ber., 1931, 64, [B], 2582—2584).—β-Thiol-β-phenylthiol-αα-diphenylethylene (this vol., 964) is isomerised in boiling ligroin to Ph diphenyldithioacetate, $CHPh_2·CS_2Ph$, m. p. 78—79°. When either substance or Ph diphenylthioacetate is heated at 250—280°, PhOH or PhSH is removed with production of dimeric diphenylthioketen,

$$CPh_2{:}C{<}^S_S{>}C{:}CPh_2,$$ m. p. 257—258°. Hydrolysis of Ph diphenyldithioacetate with aq. H_2SO_4 in AcOH yields diphenylacetic acid, m. p. 146°. H. Wren.

Organic compounds of sulphur. XX. Sulphur analogues of hexaphenylethane. II. A. Schönberg, D. Cernik, and W. Urban (Ber., 1931, 64, [B], 2577—2581; cf. A., 1930, 1577).—Contrary to Bergmann (A., 1930, 1584), the action of thiobenzophenone on diazomethane in Et_2O yields the colourless 4:4:5:5-tetraphenyltrimethylene 1:3-disulphide, $CH_2{<}^{S·CPh_2}_{S·CPh_2}$, m. p. 199—200°, converted by LiPh into $CPh_3{·}CPh_2$. Below its m. p. it commences to decompose into thiobenzophenone, S, and $CH_2{:}CPh_2$. Similarly, thiobenzophenone is converted by diazoethane and Et diazoacetate into 2-methyl-4:4:5:5-tetraphenyltrimethylene 1:3-disulphide, m. p. 170—172°, and 2-carboxyethyl-4:4:5:5-tetraphenyltrimethylene 1:3-disulphide, respectively. These compounds, particularly that last-named, which decomposes in indifferent media at room temp. particularly in presence of light, are more thermolabile than the parent substance. Thiobenzophenone and diphenyldiazomethane afford tetraphenylethylene sulphide; it is assumed that 2:2:4:4:5:5-hexaphenyltrimethylene 1:3-trisulphide is intermediately formed, but is too unstable to permit isolation. H. Wren.

Derivatives of phenacyl sulphides and their properties. A. Kretov, A. Pantchenko, and A. Konovaltchik (J. Gen. Chem. Russ., 1931, 1, 396—400).—The action of Na_2S on ω-chlorodimethylacetophenone gives dimethylphenacyl sulphide (decomp. above 100°), of which the dioxime was not obtained. The dioxime of p-methylphenacyl sulphide has m. p. 149—150°, and the monophenylhydrazone, m. p. 137°. Bromination of phenacyl sulphide in

cold glacial AcOH gives the dibromide, m. p. 101°. On further bromination and heating, decomp. takes place, BzOH being formed. Phenacyl mercaptan (an oil, distils under reduced pressure) is prepared by the action of $Na_2S_2O_3$ on ω-chloroacetophenone. Derivatives of phenacyl sulphides are analogous to the parent substances and give ketone reactions, but with greater difficulty. E. B. Uvarov.

Structures of enol-acetates and the corresponding vinylamines. L. J. Roll and R. Adams (J. Amer. Chem. Soc., 1931, 53, 3469—3476).—Reduction of Et β-acetoxycrotonate (the enol-acetate of Et acetoacetate) in presence of PtO_2–Pt-black and AcOH gives Et butyrate. The enol-acetate, b. p. 120—122°/2 mm., of benzoylacetone has the structure $CHBz{:}CMe·OAc$, since it is reduced similarly to butyrophenone. The enol-acetate, b. p. 130—133°/2 mm., of α-phenylpentane-αγ-dione is reduced to a mixture of phenylbutylcarbinol and its acetate; the mixture is oxidised (after hydrolysis) by $K_2Cr_2O_7$ and dil. H_2SO_4 to valerophenone, which when reduced catalytically yields a similar mixture. Similarly, the enol-acetate, b. p. 136—139°/2 mm., of α-phenylhexane-αγ-dione affords a mixture of phenylamylcarbinol and its acetate, which on hydrolysis and oxidation yields Ph amyl ketone. Catalytic reduction of Et β-aminocrotonate in AcOH gives Et β-acetamidobutyrate, which on hydrolysis and subsequent distillation furnishes Et crotonate. Et n-butylacetoacetate and NH_3 in EtOH afford Et β-amino-α-n-butylcrotonate, m. p. 31°, reduced catalytically (as above) in AcOH to Et β-acetamido-α-butylbutyrate, b. p. 158—160°/3 mm. β-Amino-α-butylbutyric acid (hydrochloride, m. p. 87—88°) passes at 220° into α-butylcrotonic acid, b. p. 160—163°/23 mm. H. Burton.

Benzanthrone derivatives. I. New synthesis of benzanthrone derivatives. II. Derivatives of bromobenzanthrone. M. Nakanishi (Bull. Inst. Phys. Chem. Res. Tokyo, 1931, 10, 883—896, 897—908).—I. Anthrone is condensed with crotonaldehyde to compounds, $C_{18}H_6O_2$, m. p. 242°, and $C_{18}H_{14}O$, m. p. 125—127°, both of which are converted by Br into γ:9-dibromo-9-butenyl-10-anthrone, $C_{18}H_{14}OBr_2$, $CO{<}^{C_6H_4}_{C_6H_4}{>}CBr·CH{:}CH·CHMeBr$, m. p. 136°. The dibromide is oxidised by $KMnO_4$ to 9-bromo-10-anthrone-9-carboxylic acid, m. p. 146°, and gives by treatment with $AlCl_3$ in $PhNO_2$ at 200° compounds, $C_{18}H_9OBr$, m. p. 173°, and $C_{18}H_8OBr_2$, m. p. 258°, which yield bluish-violet vat dyes when boiled with NaOMe in MeOH, one Br atom being lost. No methylbenzanthrone is obtainable from crotonylideneanthrone itself.

II. Trinitrobenzanthrone, m. p. 247°, obtained from benzanthrone and HNO_3 of d 1·48, is stable to CrO_3 oxidation. The Bz-NO_2 group is reduced by NH_3 and H_2S, and the product, m. p. 236°, gives by CrO_3 oxidation 2:7-dinitroanthraquinone. Nitration of 3-bromobenzanthrone yields a NO_2-compound, m. p. 301—301·5°, reducible to 3-bromo-2(or 1)-aminobenzanthrone, m. p. 248—250° (Ac derivative, m. p. 278°). The bromonitro-compound is converted by PCl_5 into 2(or 1)-chloro-3-bromobenzanthrone 7:7-dichloride, m. p. 227°, and by NaOEt into a

green vat dye. The quinoline, m. p. 245°, from the bromoamino-compound gives with NaOEt an intense brownish-red vat dye. Alkaline fusion of 3-bromo-2(or 1)-nitrobenzanthrone gives a dinitrodibenzanthrone (green vat dye), whilst the bromoamine yields an azine (reddish-brown).   C. Hollins.

Manufacture of halogenated cyclic ketones of the acenaphthene series. I. G. Farbenind. A.-G., —See B., 1931, 1041.

Manufacture of ω-aminomethylbenzanthrone. I. G. Farbenind. A.-G.—See B., 1931, 1041.

Anthraquinone series. Condensation of 3 : 5-dinitrophthalic acid with toluene. P. C. Mitter and R. Goswami (J. Indian Chem. Soc., 1931, 8, 685—688).—3 : 5-Dinitrophthalic anhydride and PhMe in presence of $AlCl_3$ give 3 : 5-*dinitro*-2-p-*toluoylbenzoic acid*, m. p. 237°, reduced by $FeSO_4$ and aq. NH_3 to 3 : 5-*diamino*-2-p-*toluoylbenzoic acid*, m. p. 170—171°. This is converted by conc. H_2SO_4 at 160—170° into 1 : 3-*diamino*-6-*methylanthraquinone*, m. p. 265°, characterised by its conversion into 1 : 3-dihydroxy-6-methylanthraquinone.   H. Burton.

1 : 3-Dichloroanthraquinone. A. A. Goldberg (J.C.S., 1931, 2829—2830).—Phthalic anhydride condenses with *m*-dichlorobenzene to give dichlorobenzoylbenzoic acid, which in 5% oleum at 155—160° forms 1 : 3-dichloroanthraquinone, m. p. 209—210°.   F. R. Shaw.

Synthesis of alizarin. V. I. Minaev and B. P. Federov (Bull. Inst. polytech. Ivanovo-Vosniesensk, 1930, 15, 113—130).—Anthracene is chlorinated in o-$C_6H_4Cl_2$, yielding 90% of very pure 9 : 10-dichloroanthracene, which is sulphonated with oleum in $PhNO_2$; $PhNO_2$ is removed with steam and the 9 : 10-dichloroanthracene-2-sulphonic acid converted quantitatively with HNO_3 (d 1·2) into anthracene-2-sulphonic acid, which yields very pure alizarin in quant. yield on alkaline oxidative fusion.

Chemical Abstracts.

3-Iodoalizarin. A. G. Perkin and C. W. H. Storey (J.C.S., 1931, 2620—2624).—2-Hydroxy-(Hardacre and Perkin, A., 1929, 319) and 2 : 7-dihydroxy- are the only 2-hydroxy-anthraquinones with the 3-position free which are iodinated in pyridine, the latter giving 3-*iodo*-2 : 7-*dihydroxyanthraquinone*, m. p. 305—307° (Ac_2 derivative, m. p. 218—221°). Alizarin is inert, but alizarin 1-Me ether is converted into 3-*iodoalizarin* 1-*Me ether*, m. p. 235—237°, demethylated to 3-*iodoalizarin*, m. p. 227—229° (*Ac* derivative, m. p. 205—207°), which dyes yellower shades than alizarin. Iodination of 1-bromo-2-hydroxyanthraquinone gives the 3-iodo-2-hydroxy-compound (I) with elimination of Br; but when excess of I is used, a red *substance*, m. p. 289—290°, is produced, related to, but not formed by the action of I on, (I).   F. R. Shaw.

Polycyclic aromatic hydrocarbons. VI. 3 : 4-Benzphenanthrene and its quinone. VII. 5 : 6-*cyclo*Penteno-1 : 2-benzanthracene, a cancer-producing hydrocarbon. J. W. Cook (J.C.S., 1931, 2524—2528, 2529—2532).—VI. The Pschorr synthesis with α-(2-naphthyl)-*o*-aminocinnamic acid (cf. A., 1912, i, 547) gives a mixture of 1 : 2-*benz*-4-

anthroic acid (I), m. p. 281—282°, and 3 : 4-*benz*-1-*phenanthroic acid* (II), m. p. 240—241°, separated through the Na and K salts. When oxidised with CrO_3, (I) affords 1 : 2-*benzanthraquinone*-4-*carboxylic acid*, m. p. 292—293° (decomp.), which passes into the quinone on heating, whilst (II) is converted into 3 : 4-*benz*-9 : 10-*phenanthraquinone*, m. p. 187—188°, which reacts readily with *o*-phenylenediamine to form 1 : 2-*benz*-3 : 4-(1′ : 2′-naphtha)phenazine, m. p. 189—190°. (I) is converted by Cu powder into 3 : 4-*benzphenanthrene*, m. p. 68°, purified through its *picrate*, m. p. 126—127°. 1 : 2-Benzanthracene picrate, m. p. 141·5—142·5°, contains 1 mol. of picric acid (cf. Elbs, A., 1886, 1037).

VII. 5 : 6-*cyclo*Penteno-1 : 2-benzanthracene (III) (this vol., 612) (*picrate*, m. p. 195°; *quinone*, m. p. 184·5—185·5°) shows pronounced cancer-producing activity. The isomeric 6 : 7-cyclopenteno-1 : 2-*benzanthracene*, m. p. 164—165° (*quinone*, m. p. 182—184°), purified through its *picrate*, m. p. 180°, is formed at the same time. The constitution of (III) is proved by the oxidation of the quinone to *anthraquinone*-1 : 2 : 5 : 6-*tetracarboxylic acid*, m. p. above 360° (Me_4 ester, m. p. 292—293°), identical with that obtained from 1 : 2 : 5 : 6-dibenzanthraquinone.   F. R. Shaw.

Constitution of corchoritin, a new crystalline bitter [substance] from jute seeds. I. N. K. Sen (J. Indian Chem. Soc., 1931, 8, 651—665).—The mother-liquors from the crystallisation of corchorin (A., 1930, 826; this vol., 337) contain a little *corchoritin* (I), $C_{12}H_{18}O_3$ ($+0·5H_2O$), m. p. (anhyd.) 218—220° (decomp.) (sinters at 130°), $[α]_D^{17}$ (anhyd.) $-35·1°$ in EtOH (*monoacetate*, m. p. 120—122°; *phenylurethane*, m. p. 254—266°). (I) is unsaturated, is not a glucoside, contains a lactone grouping, does not give an oxime, and when hydrolysed with EtOH–KOH affords, after acidification with AcOH, a small amount of a *substance*, m. p. 182° (decomp.), isomeric with (I). Treatment of (I) with conc. HCl at room temp. gives *anhydrocorchoritin*, m. p. 97—98° (decomp.), whilst catalytic reduction (Pd) in MeOH affords *dihydrocorchoritin*, m. p. 191°. Distillation of (I) with Zn dust in H_2 yields gaseous and liquid products together with a $C_{10}H_8$-like *substance*, m. p. 135° [*picrate*, m. p. 107°; NO_2-derivative (?), m. p. 150° (decomp.)], whilst oxidation with alkaline $KMnO_4$ gives AcOH, oxalic and pyruvic acids. *o*-Phenylenediamine hydrochloride and (I) in AcOH give a blood-red coloration; the reaction is used for detecting traces of (I).   H. Burton.

Constitution of bile-pigments. VI. Synthesis of mesobilirubinogen, neobilirubic acid, mesobilirubin, a neoxanthobilirubic acid, and 1 : 8-dihydroxytripyrrodienes. H. Fischer and E. Adler (Z. physiol. Chem., 1931, 200, 209—231; cf. this vol., 967).—Me xanthobilirubate gives with SO_2Cl_2 a colourless Cl_6-derivative, decomp. 167°; the free acid does not yield a cryst. derivative. Bromination of bilirubic acid with 1 mol. of Br gives xanthobilirubic acid (I), which on bromination yields mesobilirubin (II) (as hydrobromide) (mesobilirubin ester, m. p. 216°). Reduction of (II) with Na–Hg affords mesobilirubinogen, with HI in AcOH neo-

bilirubic acid (III) and bilirubic acid, fusion with resorcinol neoxanthobilirubic acid (IV). Reduction of (IV) with Na–Hg gives (III). Condensation of (IV) with CH_2O gives (II). Bromination of (I) at −20° also gives (II), which is unchanged by HBr in AcOH. Bromination of (I) gives as by-product an *isomeride* of (II), m. p. 305—310° (decomp.), absorption bands at 695 and 635 mμ (*Me ester hydrochloride*, m. p. 235—240°). Resorcinol fusion and Na–Hg reduction give the same products as those obtained from (II).

Bromination of 5-hydroxy-3 : 3′ : 5′-trimethyl-4-ethyl-4′-β-carboxyethylpyrromethene yields a meso-bilirubin *isomeride*, decomp. 327° (*Me* ester, m. p. 222°). 5-Carboxy-2-formyl-4-methyl-3-β-carboxy-ethylpyrrole with cryptopyrrole and HBr gives the unstable 5-*carboxy*-4 : 3′ : 5′-*trimethyl*-4′-*ethyl*-3-β-*carboxyethylpyrromethene hydrobromide*, which with $CH_2Br·CO_2H$ gives 5-*bromo*-4 : 3′ : 5′-*trimethyl*-4-*ethyl*-3-β-*carboxyethylpyrromethene hydrobromide* (V), m. p. 160° (decomp.). KOAc with (V) yields 5-*hydroxy*-4 : 3′ : 5′-*trimethyl*-4-*ethyl*-β-*carboxyethylpyrromethene*, m. p. 282°. 5-*Hydroxy*-3-*carbethoxy*-4-*methyl*-2-*chloromethylpyrrole* (VI) condenses with opsopyrrole (boiling C_6H_6) to form 1 : 8-*dihydroxy*-3 : 6-*dicarbethoxy*-2 : 4 : 7-*trimethyl*-5-*ethyltripyrrene*, m. p. 283° (decomp.). (VI) condenses with opsopyrrolecarboxylic acid forming 1 : 8-*dihydroxy*-3 : 6-*dicarbethoxy*-2 : 4 : 7-*trimethyl*-5-β-*carboxyethyltripyrrene*, m. p. 245°. (VI) heated in boiling MeOH with opsopyrrole gives 5-*hydroxy*-3-*carbethoxy*-4 : 3′-*dimethyl*-4′-*ethyl*-*pyrromethene*, m. p. 210°, which condenses with PhCHO to form [*di*-(5-*hydroxy*-3-*carbethoxy*-4 : 3′-*dimethyl* - 4′ - *ethyl*)*pyrromethene*]*phenylmethane*, absorption bands 640 and 530 mμ.   J. H. BIRKINSHAW.

New source of hydrocarotene. O. RYGH, A. RYGH, and P. LALAND (Z. physiol. Chem., 1931, **200**, 261—262).—Hydrocarotene was isolated in small amount from the juice of citrus fruits. It had no antiscorbutic action.   J. H. BIRKINSHAW.

α- and β-Carotene. R. KUHN and E. LEDERER (Z. physiol. Chem., 1931, **200**, 246—254).—Carotene isolated from ovaries, grass, spinach, or nettles contained none of the α-form. In the leaf of germinating seeds and in evergreens the β-form predominated. The two forms were not separable by fractional crystallisation, but repeated precipitation of the β-form with I led to the isolation of the pure α-form, $[\alpha]_D^{20}$ +364°, absorption bands at 511 and 478 mμ. Both forms show autoxidation at about the same rate. The ratio of the solubilities in C_6H_6 at 0° is α : β=3 : 1. The rotation of α-carotene in C_6H_6 is independent of concentration, but varies with the solvent.   J. H. BIRKINSHAW.

α-Carotene from palm oil. R. KUHN and H. BROCKMANN (Z. physiol. Chem., 1931, **200**, 255—258).—The carotene of palm oil shows the greatest optical activity of all natural carotene mixtures. Pure α-carotene was separated from the mixture by adsorption of the β-carotene on fuller's earth.
   J. H. BIRKINSHAW.

**Elasticity of guttapercha hydrocarbon.** A. W. K. DE JONG (Rec. trav. chim., 1931, **50**, 1011—1017).—Thin films of guttapercha hydrocarbon obtained by slow evaporation of a C_6H_6 solution consist of microscopic rosettes of needles, and, after stretching, show straight extinction with polarised light between crossed Nicols. The changes during gradual stretching have been examined microscopically. Films obtained by rapid evaporation from light petroleum solutions were also examined.
    J. W. BAKER.

Autoxidation of αβ-unsaturated ketones. III. Degradation and constitution of piperitolenic acid. W. TREIBS (Ber., 1931, **64**, [*B*], 2545—2552; cf. this vol., 1299).—Treatment of the lactone, m. p. 26—28°, obtained by the autoxidation of piperitone (this vol., 94) with MeOH and H_2SO_4 affords *Me piperitolenate*, b. p. 212—215°, slowly oxidised by boiling HNO_3 (*d* 1·26) to a compound containing N and finally to *iso*propylsuccinic acid. Gentle oxidation of it with $KMnO_4$ does not permit the isolation of the expected dihydroxydihydro-acid, whereas more drastic oxidation affords the *Me H* ester of the ketodicarboxylic acid (I) [*semicarbazone*, m. p. 165°
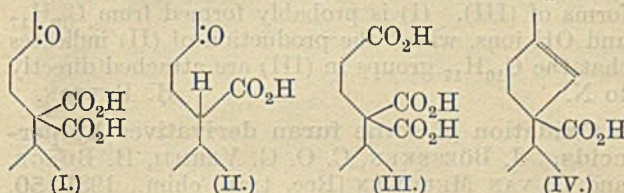
(decomp.)], converted when heated in vac. into the *Me* ester of the ketomonocarboxylic acid (II), b. p. 113°/13 mm. (*semicarbazone*, m. p. 128—130°). The free ketodicarboxylic acid (I) is oxidised by alkaline NaOBr to CBr_4 and the *tricarboxylic acid* (III), m. p. 160—162° (decomp.), whereas, under like conditions, the ketocarboxylic acid (II) affords α-*iso*propyl-glutaric acid, m. p. 95°. To piperitolenic acid the constitution (IV) is therefore ascribed. The lactone of m. p. 26—28° (see above) is converted by boiling HNO_3 (*d* 1·15) into a substance containing N and finally into AcOH, *iso*butyric, oxalic, and *iso*propylsuccinic acid, and a *tricarboxylic acid* (V), m. p. 169—170° (decomp.), which yields an *anhydride*, m. p. 145—146°. The course of the autoxidation of piperitone in presence of alkali is represented by the scheme :
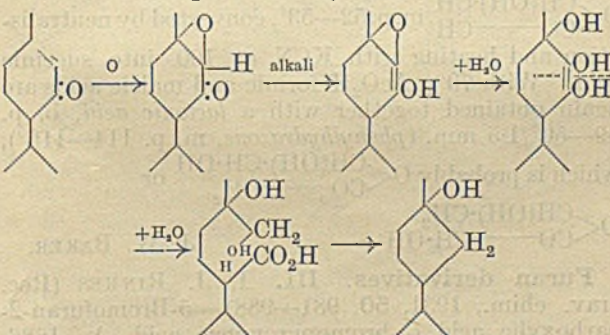
Protracted heating of piperitolenic acid at its b. p. does not cause loss of CO_2, whereas after addition of solid KOH it gives an unsaturated *hydrocarbon*, b. p. 154°, which resinifies when preserved.
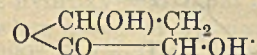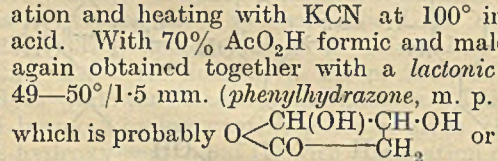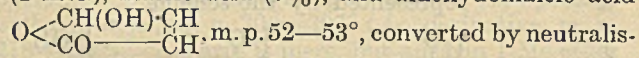   H. WREN.

Isomerisation of pinene in presence of alumina. P. A. MULCEY (Bull. Inst. Pin, 1931, 177—181, 201—206).—No camphene is obtained by the action of Al_2O_3 on pinene at its b. p. Pinene vapour, passed over Al_2O_3 at 310—425°, gives dipentene and much smaller amounts of *l*-limonene, α-terpinene, terpinolene, and light C_6H_6 hydrocarbons. No camphene is detectable. C. HOLLINS.

Preparation of bornyl mono- and di-hydrogen orthophosphates. K. P. JACOBSOHN and L. JACOBSOHN (Compt. rend. Soc. biol., 1930, **105**, 154—156; Chem. Zentr., 1931, i, 3363).—Neuberg's method (A., 1928, 88) gives both compounds; $(C_{10}H_{17})_2HPO_4$ has m. p. 221°. A. A. ELDRIDGE.

Structure of ferrocyanides. H. W. POST (J. Amer. Chem. Soc., 1931, **53**, 3904—3905).—The formation of *iso*borneol (I) and *iso*bornylamine (II) during alkaline hydrolysis of compounds of the type $(C_{10}H_{17})_2H_2Fe(CN)_6$ (III) (this vol., 736) appears to involve the existence of completely and partly ionised forms of (III). (I) is probably formed from $C_{10}H_{17}$ and OH ions, whilst the production of (II) indicates that the $C_{10}H_{17}$ groups in (III) are attached directly to N. H. BURTON.

Oxidation of some furan derivatives by per-acids. J. BÖESEKEN, C. O. G. VERMJI, H. BUNGE, and C. VAN MEEUWEN (Rec. trav. chim., 1931, **50**, 1023—1034).—The initial stage in the oxidation of furan derivatives with peracids is the formation of an oxide at one of the double linkings, and this then polymerises (especially in AcOH) or is hydrated and further oxidised. Furan with 6—10% AcO_2H in AcOH gives only an amorphous resin, $(C_4H_5O_2)_n$, mol. wt. 780, but with BzO_2H in $CHCl_3$ the *monobenzoate*, m. p. 98—100°, of 1 : 2-dihydroxy-1 : 2-dihydrofuran is obtained. With 70% AcO_2H in AcOH, 2-methylfuran affords 5-*keto*-4-*hydroxy*-2-*methyl*-4 : 5-*dihydrofuran*, m. p. 87—89° (*phenylhydrazidephenylhydrazone*, m. p. 109—110°) (together with 90% resinification), whilst furfuryl alcohol gives 5-*keto*-4 : 5-*dihydrofuran*, m. p. 150—153° (4%), (?) 5-*keto*-2-*hydroxymethyl*-2 : 5-*dihydrofuran*, b. p. 55°/0·5 mm. (12·5%), and 80% resinification. Oxidation of furfuraldehyde (1 mol.) with 6—10% AcO_2H (2 mols.) gives HCO_2H (1 mol.), maleic acid (7%), and aldehydomaleic acid

$$O{<}^{CH(OH)\cdot CH}_{CO\underline{\quad\quad}CH}, m.\ p.\ 52—53°,$$

converted by neutralisation and heating with KCN at 100° into succinic acid. With 70% AcO_2H formic and maleic acids are again obtained together with a *lactonic acid*, b. p. 49—50°/1·5 mm. (*phenylhydrazone*, m. p. 114—116°), which is probably $O{<}^{CH(OH)\cdot CH\cdot OH}_{CO\underline{\quad\quad}CH_2}$ or

$$O{<}^{CH(OH)\cdot CH_2}_{CO\underline{\quad\quad}CH\cdot OH}\cdot$$ J. W. BAKER.

Furan derivatives. III. I. J. RINKES (Rec. trav. chim., 1931, **50**, 981—988).—5-Bromofuran-2-carboxylic acid (5-bromopyromucic acid, A., 1886, 446) with HNO_3 (d 1·51) in Ac_2O at —10° gives 2-*bromo*-5-*nitrofuran*, b. p. 118°/15 mm., m. p. 48°, converted by activated Cu powder at 190° into 5 : 5′-*dinitro*-2 : 2′-*difuryl*, m. p. 213—214°, identical with the by-product obtained in the nitration of furan

(A., 1905, i, 224). Decarboxylation of 3-nitro-2-methylfuran-5-carboxylic acid (I) (this vol., 95) affords 3-*nitro*-2-*methylfuran*, f. p. 8·0°, which with HNO_3 and H_2SO_4 gives a small yield of 3 : 5-*dinitro*-2-*methylfuran*, m. p. 74°, best obtained by similar nitration of (I). 2-Nitro-3-methylfuran (*loc. cit.*) is converted by HNO_3 (d 1·2) at 100° into the 2 : 5-$(NO_2)_2$-compound, m. p. 89—90°. Et 3-methylfuran-2-carboxylate with HNO_3 and Ac_2O at —10° gives the 5-NO_2-derivative, m. p. 61°, the free *acid*, m. p. 160°, of which is decarboxylated to 5-*nitro*-3-*methyl-furan*, m. p. 291°. J. W. BAKER.

Orientation in the furan nucleus. H. GILMAN and G. F. WRIGHT (Iowa State Coll. J. Sci., 1931, **5**, 85—88).—Di-iodofuran can be prepared from dehydromucic acid and converted into a Grignard reagent by treatment with activated Mg–Cu alloy; this renders possible the substitution of a variety of radicals on the furan ring. The following compounds have been prepared : *Et* 5-*acetamido*-3(4)-*bromofuroate*, m. p. 112°; *Et* 5-*acetamido*-3(4)-*nitrofuroate*, m. p. 138°; 5-*iodo*-2-*furoic acid*, m. p. 192°. CHEMICAL ABSTRACTS.

Catalytic hydrogenation of furfuraldehyde. R. L. VAN PEURSEM (Proc. Iowa Acad. Sci., 1930, **37**, 225).—With Ni the max. yield (5%) of furfuryl alcohol is obtained at 200°, and with Cu at 215°. CHEMICAL ABSTRACTS.

Mechanisms of addition and substitution reactions of furfuraldehyde and its derivatives. H. GILMAN, G. F. WRIGHT, J. B. DICKEY, and A. P. HEWLETT (Proc. Iowa Acad. Sci., 1930, **37**, 247—248).—Substitution is preceded by 1 : 2-, 1 : 4-, or 1 : 6-addition. Ring fission, ring closure, and rearrangement involving unsaturated linkings accompany some of the transformations. CHEMICAL ABSTRACTS.

Cannizzaro reaction with furfuraldehyde. H. GILMAN and W. M. SELBY (Iowa State Coll. J. Sci., 1930, **5**, 15—18).—Yields are recorded. CHEMICAL ABSTRACTS.

Polymeric 2-furfuryl mercaptan. H. GILMAN and A. P. HEWLETT (Iowa State Coll. J. Sci., 1930, **5**, 19—23).—In 1 year a white solid, m. p. 135°, probably $(C_5H_6OS)_7$, was obtained. When kept, Et furoate is gradually converted into a substance of higher b. p. Furan compounds tend to remain unchanged when highly purified and preserved in sealed containers. CHEMICAL ABSTRACTS.
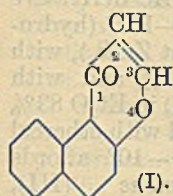
Coumaryl-6-thiocarbimide. B. B. DEY and T. R. SESHADRI (J. Indian Chem. Soc., 1931, **8**, 527—530).—6-Aminocoumarin (I) and boiling CS_2 in EtOH slowly, or with a little S more rapidly, give 6 : 6′-*di-coumarylthiocarbamide* (II), m. p. 250—252°. This with boiling Ac_2O gives *coumaryl*-6-*thiocarbimide* (III), m. p. 186—187°, and 6-acetamidocoumarin. When treated with $CSCl_2$ in dry C_6H_6, (I) forms an unstable substance, probably the thiocarbamyl chloride, which with H_2O gives the hydrochloride of (II) and (III), which was better obtained from $CSCl_2$ and (I) (3 mols.) in aq. suspension at 60°. (III) is slowly transformed into (I) by AcOH, and on boiling with (I) in EtOH gives (II). *Coumaryl*-6-*thiocarbamide*, m. p. 234—235° (decomp.), is formed from (III) and

aq. NH_3 in boiling EtOH. *Phenyl-6-coumarylthio-carbamide*, m. p. 169—170° (decomp.), obtained from (*a*) (III) and NH_2Ph, and (*b*) PhNCS and (I) in boiling EtOH or C_6H_6, decomposes into (I) on melting. With $NH_2 \cdot NHPh$ in boiling C_6H_6 (III) gives *phenyl-6-coumarylthiosemicarbazide*, m. p. 171—172°, and with boiling EtOH *Et coumaryl-6-thiocarbamate*, m. p. 167—168°. With boiling PhMe and $AlCl_3$ (I) yields 6-*thio*-p-*toluamidocoumarin*, m. p. 253—254°. The following compounds were prepared by similar methods : 6 : 6'-*di*-(4 : 7-*dimethylcoumaryl*)-, m. p. 258—260° ; 4 : 7-*dimethylcoumaryl*-, m. p. 241° (decomp.), *phenyl-4 : 7-dimethylcoumaryl-thiocarbamide*, m. p. 192° (decomp.) ; 4 : 7-*dimethylcoumaryl-6-thiocarbimide*, m. p. 235°. R. S. Cahn.

Chromone group. IV. 1 : 4-βα-Naphthapyrones. B. K. Menon and K. Venkataraman (J.C.S., 1931, 2591—2596).—1 : 4-βα-*Naphthapyrone* (I), m. p. 103°, is obtained when the oxymethylene ketone from 1-acetyl-β-naphthol (II) and Et formate is treated with H_2SO_4 in EtOH. Treatment of (II) with Ac_2O and NaOAc at 170° gives 2-acetyl-3-methyl-1 : 4-βα-naphthapyrone, converted by NH_3 in EtOH into 3-methyl-1 : 4-βα-naphthapyrone, m. p. 168° (lit. 164°). 2-Acylation does not occur with aromatic anhydrides ; βα-naphthaflavone, 4'-*methoxy*- (III), m. p. 165°, and 3' : 4' : 5'-*trimethoxy*-, m. p. 159°, -βα-*naphthaflavones* are prepared in poor yield from Bz_2O, anisic and trimethylgallic anhydrides, respectively. 4'-*Methoxy*-, m. p. 143°, 3' : 4'-*dimethoxy*-, m. p. 157°, and 3' : 4'-*methylenedioxy*-, m. p. 169°, -βα-*naphthaflavanones*, prepared from (II) and anisaldehyde, veratraldehyde, and piperonal, respectively, in presence of aq. EtOH–NaOH, are converted by PCl_5 in C_6H_6 into (III), 3' : 4'-*dimethoxy*-, m. p. 168°, and 3' : 4'-*methylenedioxy*-, m. p. 225—226°, -βα-*naphthaflavones*, respectively. 4'-*Hydroxy*- and 3' : 4'-*dihydroxy-βα-naphthaflavones*, prepared by demethylation of the corresponding OMe-derivatives, have m. p. 283—285° and 302—304°, respectively. Colour reactions of these substances are given. H. Burton.

Synthesis of anthocyanins. VI. Synthesis of chrysanthemin chloride. S. Murakami, A. Robertson, and R. Robinson. **VII. Four isomeric β-glucosides of pelargonidin chloride.** A. León, A. Robertson, R. Robinson, and T. R. Seshadri. **VIII. Synthesis of oenin chloride.** L. F. Levy, T. Posternack, and R. Robinson. **IX. Synthesis of oxycoccicyanin chloride. Distribution number of anthocyanins.** L. F. Levy and R. Robinson. **X. Synthesis of 3-β-galactosidylcyanidin chloride, which is believed to be identical with idæin chloride, and of 3-β-galactosidylpeonidin chloride.** (Miss) K. E. Grove and R. Robinson. **XI. Fisetinin chloride.** E. L. Fonseka and R. Robinson. **XII. Fisetinidin and luteolinidin chlorides.** A. León and R. Robinson. **XIII. 5-β-Glucosidyl- and 5-lactosidyl-hirsutidin chlorides.** L. F. Levy and R. Robinson (J.C.S., 1931, 2665—2671, 2672—2701, 2701—2715, 2715—2722, 2722—2730, 2730—2732, 2732—2737,

2738—2742 ; cf. A., 1928, 895).—VI. Chrysanthemin chloride (I) is shown by synthesis to be 3-β-glucosidyl-cyanidin chloride. Mecocyanin chloride is 3-(glucosidylglucosidyl)cyanidin chloride, since it resembles (I) in colour reactions and yields (I) on hydrolysis. Similarly, keracyanin and prunicyanin are probably 3-biosides. Cyanin (II), peonin, pelargonin, and malvin may, however, be diglucosides. (II) is considered to be probably cyanidin 3 : 5-diglucoside because of its resemblance to fisetinin chloride in colour reactions, its stability to oxidising agents, and its partial hydrolysis. The Na_2 salt of ω-chloro-3 : 4-dihydroxyacetophenone (improved prep.) with Ac_2O in cold C_6H_6 gives ω-*hydroxy*-3 : 4-*diacetoxyacetophenone* (III), m. p. 86—87° (reduces cold Fehling's solution in presence of a little EtOH), isolated as $CaCl_2$ *compound*, $2C_{12}H_{12}O_6,CaCl_2$, m. p. 126—127°, from which it is regenerated by H_2O. (III) with O-tetra-acetyl-α-glucosidyl bromide and Ag_2CO_3 in dry $CHCl_3$ gives ω-O-*tetra-acetyl-β-glucosidoxy-3 : 4-diacetoxyacetophenone*, m. p. 105—105·5°, which, when condensed with O-benzoylphloroglucin-aldehyde and HCl in dry $CHCl_3$–EtOH or EtOAc, hydrolysed by NaOH, treated with HCl, and subsequently with picric acid, affords 3-β-*glucosidoxy-5 : 7 : 3' : 4'-tetrahydroxyflavylium picrate*, $+4H_2O$, m. p. 170—175° or higher according to the rate of heating (vigorous decomp. 190—193°), identical with the picrate prepared from " asterin " chloride and chrysanthemin chloride, and converted by HCl in MeOH into the corresponding *chloride*, identical in crystal form, solubility, distribution no., and colour reactions in buffered solutions with natural chrysanthemin chloride from four different sources.

VII. The 5-, 7-, and 4'-β-glucosides of pelargonidin chloride are synthesised (cf. *loc. cit.*), and the first mentioned is identified with pelargonenin chloride, which differs from the other glucosides in colour reactions. Pelargonin is pelargonidin 3 : 5-di-glucoside, since it is stable to very dil. aq. $FeCl_3$; its methylation (A., 1928, 1255) and that of monardein are discussed on the basis of this constitution. 6-Orcylaldehyde, ω-hydroxy-p-acetoxyacetophenone (I), and HCl in dry EtOAc give 3 : 7 : 4'-*trihydroxy-5-methylflavylium chloride*, $+H_2O$, and a small amount of xanthylium salt. γ-Orcylaldehyde led similarly to 3 : 5 : 4'-*trihydroxy-7-methylflavylium chloride*, $+2H_2O$. 4 : 6-Dihydroxy-2-methoxybenzaldehyde (prepared from phloroglucinol methyl ether), CH_2PhBr, and K_2CO_3 in boiling $COMe_2$ yield 2-*hydroxy-4-benzyloxy-6-methoxybenzaldehyde*, m. p. 101—102°, the constitution of which is proved by condensation with (I) to a flavylium salt. 6-Methylphloroglucinalde-hyde benzyl ether, (I), and HCl in dry EtOAc give 3 : 4'-*dihydroxy-7-benzyloxy-5-methoxyflavylium chloride*, hydrolysed by conc. HCl in hot AcOH to 3 : 7 : 4'-*trihydroxy-5-methoxyflavylium chloride*, $+1·5H_2O$. Condensation of 6-hydroxy-2-benzoyloxy-4-methoxy-benzaldehyde with (I), hydrolysis of the product with NaOH in an atm. of H_2, and subsequent treatment with HCl affords 3 : 5 : 4'-*trihydroxy-7-methoxyflavylium chloride*. ω-4-Diacetoxyacetophenone and hot aq. KOH give ω : 4-*dihydroxyacetophenone*, m. p. 177—178° after sintering at 170° [K salt (II), $+2H_2O$ (lost at 120°), turns brown at 235° and decomp. at 275° ;

Ag salt, decomp. in warm H_2O; *osazone*, m. p. 212—214°], which, when condensed with 2-*O*-benzoyl-phloroglucinaldehyde (III) (modified prep.), yields 5-*O*-benzoylpelargonidin chloride. (II) and α-tetra-acetylglucosidyl bromide (IV) in aq. $COMe_2$ give ω-*hydroxy-4-tetra-acetylglucosidoxyacetophenone*, m. p. 149—150° (reduces cold Fehling's solution and hot ammoniacal $AgNO_3$), which with (III) and HCl in dry Et_2O-$CHCl_3$ yields 5-*O*-*benzoyl-4'-O-tetra-acetylglucosidylpelargonidin chloride*, darkens at 182°, sinters at 193°, decomposes at 198°, transformed by successive treatment with NaOH and HCl into 4'-β-*glucosidylpelargonidin chloride*, $+2.75H_2O$, decomp. 184° (corresponding *picrate*, decomp. 146—148°), which gives pelargonidin chloride on hydrolysis. The *Ag* salt of (III) (modified prep.) [but not the *K* salt (decomp. above 70°)] and (IV) in dry C_6H_6 give a poor yield of 2-*benzoyl-4-β-tetra-acetylglucosidylphloroglucinaldehyde* (V), m. p. 144—145°, which was better obtained from (III), (IV), and KOH in aq. $COMe_2$. This with MeI and Ag_2CO_3 in $COMe_2$ gives 2-*benzoyl-4-β-tetra-acetylglucosidyl-6-O-methylphloroglucinalde-hyde*, m. p. about 120° after sintering at about 85°, hydrolysed by HCl in aq. EtOH at 50—60° or KOH in cold EtOH to 4-β-*glucosidyl-2-O-methylphloroglucin-aldehyde* (VI), m. p. 237—239° (decomp.) after sintering at 235° (FeCl₃ colour, brownish-red), stable to dil., but decomposed by conc., acids. 6-*O*-Benzoyl-2 : 4-*O*-dimethylphloroglucinaldehyde also loses the Bz group on treatment with HCl. The constitution of (VI) is proved by its prep. from aq. KOH and 4-β-*tetra-acetylglucosidyl-2-O-methylphloroglucinaldehyde*, m. p. 147—148° [obtained from 2-*O*-methylphloroglucin-aldehyde, (IV), and KOH in aq. $COMe_2$]. (V), ω : 4-dihydroxyacetophenone, and HCl in dry $CHCl_3$-Et_2O give 3 : 4'-*dihydroxy-5-benzoyloxy-7-β-tetra-acetylglucosidylflavylium chloride*, decomp. 184—186° after sintering at 177°, transformed by KOH in MeOH in an atm. of N_2 and subsequent treatment with HCl and picric acid into 7-β-*glucosidylpelargonidin picrate*, $+1.5H_2O$, m. p. 180° (decomp.) after sintering at 120° (corresponding *chloride*, $+3H_2O$). 2 : 4-*O*-Dibenzoyl-phloroglucinaldehyde, m. p. 139—140°, obtained as a by-product in varying yield in the prep. of the 2-*O*-Bz compound, was prepared from phloroglucin-aldehyde, BzCl, and KOH in aq. $COMe_2$ and from the 2-*O*-Bz compound by benzoylation in alkaline aq. $COMe_2$ or, better, in pyridine, and its constitution proved by methylation with MeI and Ag_2CO_3 in $COMe_2$ to 2 : 4-*dibenzoyl-6-O-methylphloroglucinalde-hyde* (VII), m. p. 133—134°, hydrolysed by aq. KOH to the 2 : 4-(OH)₂ compound. *Tribenzoylphloro-glucinaldehyde* has m. p. (anhyd.) 121—122°, and $+0.5H_2O$, m. p. 80° (rapid heating) or about 118° (slow heating) after sintering at 80°. (VII) with tetra-acetylglucosidyl bromide and Ag_2CO_3 in dry C_6H_6 gives (?) 2 : 4-*dibenzoyl-6-β-glucosidylphloroglucinalde-hyde*, m. p. 145° after sintering at 85° and becoming glassy at 110° (yields only BzOH on hydrolysis and does not give a cryst. Ac derivative), and with (IV) and KOH in aq. $COMe_2$ gives (?) 2 : 4-*dibenzoyl-6-tetra-acetyl-β-glucosidylphloroglucinaldehyde*, (?) $+3.5H_2O$, m. p. 144—145°, also obtained together with a *substance*, m. p. 224—226°, from (VI), (IV), and Ag_2O in quinoline. The product (which could not

be purified), obtained on hydrolysis of the last-mentioned aldehyde by cold alcoholic KOH in an atm. of N_2, when treated with ω-4-dihydroxyaceto-phenone and HCl in cold EtOH yields 5-β-*glucosidyl-pelargonidin chloride*, identical in m. p., solvent of cryst., crystal form, and colour reactions with pelargonenin chloride. This salt and the 4'- and 7-glucosides are decolorised by very dil. $FeCl_3$ in 1% HCl in 35 min., but callistephin, pelargonin, monardin, and salvidin chlorides were stable under these conditions. γ-Orcylaldehyde Me_2 ether, prepared by MeI and K_2CO_3 in $COMe_2$, has m. p. 91—92° (lit. 90—91°). The colour reactions of pelargonin and the 3-, 5-, 7-, and 4'-glucosides and 7- and 5-Me ethers of pelargonidin are recorded for various reagents and buffered solutions.

VIII. Oenin chloride (from purple-black grapes) and (probably) "primulin" chloride are shown by synthesis to be 5 : 7 : 4'-trihydroxy-3': 5'-dimethoxy-3-β-glucosidylflavylium chloride (3-β-glucosidylmalv-idin chloride). Syringic acid with Ac_2O and a few drops of pyridine at 100° gives little Ac derivative (I) and much *anhydride* (II), m. p. 195—197° (hydro-lysed by hot 2N-NaOH with or without $ZnCl_2$), with boiling Ac_2O much (I) and little (II), and with N-NaOH (2.5 mols.) and Ac_2O (1.5 mols.) in Et_2O 83% of (I). Acetylsyringoyl chloride treated with ethereal diazomethane in a little $CHCl_3$ at −10° affords ω-*diazo-4-acetoxy-3 : 5-dimethoxyacetophenone* (III), m. p. 134° (decomp.), which is transformed into an amorphous substance (reducing Fehling's solution) by dil. aq.-alcoholic KOH, but with AcOH at 70° yields ω : 4-*diacetoxy-3 : 5-dimethoxyacetophenone*, m. p. 123°, hydrolysed by KOH in MeOH to the corre-sponding ω : 4-(OH)₂-compound (IV), m. p. $+$?H_2O 93—95°, anhyd. 132° (*K* salt). Benzoylsyringoyl chloride (modified prep.), m. p. 125° (lit. 118°), affords the *diazo-ketone* (V) corresponding with (III), m. p. 168—172° (decomp.), which with cold abs. HCO_2H gives 4-*benzoyloxy-ω-formoxy-3 : 5-dimethoxyaceto-phenone*, cryst., and, best with hot 50% HCO_2H, yields ω-*hydroxy-4-benzoyloxy-3 : 5-dimethoxyaceto-phenone*, m. p. 175—177°. This with BzCl and pyridine gives the ω : 4-*Bz₂* compound, m. p. 128°, and with Ac_2O and a drop of pyridine ω-*acetoxy-4-benzoyloxy-3 : 5-dimethoxyacetophenone*, m. p. 143° (rapidly reduces hot Fehling's solution), also obtained from (V) and hot AcOH. The ω-OH-compound with *O*-tetra-acetyl-α-glucosidyl bromide and Ag_2O in dry C_6H_6, first at 40° and then under reflux, gives a poor yield of 4-*benzoyloxy-ω-O-tetra-acetyl-β-glucosidoxy-3 : 5-dimethoxyacetophenone*, m. p. 80—90°, whence a monoglucosidic pyrylium salt, doubtless oenin, was obtained. (III) with anhyd. HCO_2H affords ω-*formoxy-4-acetoxy-3 : 5-dimethoxyacetophenone*, m. p. 152.5°, which with boiling 50% EtOH gives ω-*hydroxy-4-acetoxy-3 : 5-dimethoxyacetophenone* (VI), $+$?H_2O, m. p. anhyd. 119—120°, also obtained from (III) and 50% HCO_2H [ω-*Bz* derivative, m. p. 158—159°, from (III) and BzOH at 110—120°, or (VI), BzCl, and pyridine]. (VI) gives, in the usual way, ω-*O-tetra-acetyl-β-glucosidoxy-4-acetoxy-3 : 5-dimethoxy-acetophenone*, m. p. 83—85° (decomp.) (possibly the Ac_3 compound), which with *O*-benzoylphloroglucin-aldehyde and HCl in dry EtOAc at 15° yields 7-*hydroxy-*

5-benzoyloxy-3-O-tetra-acetyl-β- glucosidoxy - 4' - acetoxy-3' : 5'-dimethoxyflavylium chloride, +2H_2O. This on hydrolysis with 10% aq. NaOH in an atm. of N_2 and subsequent ring-closure by HCl gives 3-β-glucosidyl-malvidin chloride, +3H_2O. This and the corresponding picrate [+1·5H_2O, or, (?) if not pure, +4H_2O] are identical in m. p., crystal form, solvent of cryst., distribution no., solubility, absorption spectrum, colour reactions in buffered solutions, and various chemical reactions with oenin derivatives. The crude anthocyanin from "Fogarina" grapes contains, besides oenin, malvidin, delphinidin, and probably petunidin.

IX. The prep. of ω-chloroacetovanillone and thence of 4-hydroxy-ω-acetoxy-3-methoxyacetophenone is improved. The latter substance with hot 16% aq. NaOH gives ω : 4-dihydroxy-3-methoxyacetophenone, + ?H_2O, m. p. 158—160° (Na salt, +1·5H_2O) (reduces cold Fehling's solution). The 4-Ac derivative of this, m. p. +0·5H_2O 88—90°, anhyd. 96°, prepared by shaking the aq. suspension with Ac_2O (1·5 mols.) in $CHCl_3$ (reduces cold Fehling's solution, gives no colour with $FeCl_3$, and insol. in NaOH, whereby its constitution is proved), affords the ω : 4-Ac_2 derivative, m. p. 76° (lit. 73°), when heated with Ac_2O, and when condensed with O-tetra-acetyl-α-glucosidyl bromide in the usual way yields ω-O-tetra-acetyl-β-glucosidoxy-4-acetoxy-3-methoxyacetophenone, m. p. 74—76° (possibly partly deacetylated), which with 2-O-benzoylphloroglucinaldehyde and HCl in EtOAc gives 7-hydroxy-5-benzoyloxy-3-O-tetra-acetylglucosidoxy-4'-acetoxy-3'-methoxyflavylium chloride, +1·5H_2O (possibly an Ac_2 compound), whence by hydrolysis and subsequent ring closure 3-β-glucosidylpeonidin chloride, +2H_2O, and the corresponding picrate, +4·5H_2O, decomp. 165—180° after darkening at 110°, were obtained. These are identical with the corresponding salts of oxycoccicyanin. The glucoside is affected by $FeCl_3$ less than oenin, but more than callistephin; it is stable to very dil. $FeCl_3$, whereas peonidin is rapidly oxidised. The distribution nos. of oxycoccicyanin, natural and synthetic oenin chlorides between amyl alcohol and H_2O at different concentrations indicate that the anthocyanins exist as double mols. in the latter and single mols. in the former solvent; this is possibly connected with the difficulty of cryst. of anthocyanins and anthocyanidins from aq. acids and with the blueing effect of tannin on oenin solutions.

X. ω-Hydroxy-3 : 4-diacetoxyacetophenone (modified prep.), m. p. 86—87°, O-tetra-acetyl-α-galactosidyl bromide, and Ag_2CO_3 in warm dry C_6H_6 give the ω-O-tetra-acetyl-β-galactoside, amorphous, which with O-benzoylphloroglucinaldehyde and HCl in dry EtOAc yields 7 : 3' : 4'-trihydroxy-5-benzoyloxy-3-β-galactosidoxyflavylium chloride, transformed by 8% aq. NaOH and subsequent acidification into 3-β-galactosidylcyanidin chloride (I), +H_2O, identical with idæin chloride. ω-Hydroxy-4-acetoxy-3-methoxy-acetophenone gives similarly the ω-O-tetra-acetyl-β-galactoside, 7 : 4'-dihydroxy-5-benzoyloxy-3-β-galactosidoxy 3' - methoxyflavylium chloride, amorphous, +2H_2O, and 3-β-galactosidylpeonidin picrate +H_2O, and chloride (II), +2·5H_2O. The absorption curves (visible region) and alkali colour reactions are identical

for (I) and oxycoccicyanin chloride (III), and for (II) and chrysanthemin chloride (IV), whilst the distribution nos. are controlled more by the carbohydrate component, being almost identical for (I) and (II), and for (III) and (IV). According to distribution experiments, association occurs between (I) and (IV) when mixed in aq. solution.

XI. The alkali colour reactions of 3-β-glucosidyl-fisetinidin chloride (I), which has been synthesised, are similar to those of cyanin chloride, thus confirming the diglucoside structure of the latter. In the cyanidin, peonidin, and malvidin, but not always in the pelargonidin, series, substitution in position 3 has a large effect on these colour reactions only if the OH group in position 5 is free. ω-Hydroxy-3 : 4-diacetoxy-acetophenone, O-tetra-acetylglucosidyl bromide, and Ag_2CO_3 in warm C_6H_6 give the ω-tetra-acetyl-β-glucoside, which with β-resorcylaldehyde and HCl in dry EtOAc at 0° yields the flavylium salt, transformed by 8% NaOH in an atm. of H_2 and subsequent acidification into fisetinin chloride [=(I)], +1·5H_2O (corresponding picrate, +5H_2O), generally similar to chrysanthemin chloride.

XII. Under standard conditions, luteolinidin (I), fisetinin (II), chrysanthemin, cyanin, malvin, and oenin chlorides (which do not possess a free OH group in position 3) are stable to $FeCl_3$, whilst cyanidin, fisetinidin, cyanidin 5-glucoside (III), and malvin 5-glucoside (in which the OH in position 3 is free) are unstable; the 3 : 5-diglucoside structure for cyanin is thus confirmed. (I) and (II) have been synthesised in a pure state and solutions of (III) have been prepared by two methods. By the Schotten–Baumann method β-resorcylaldehyde yields the 4-Bz derivative, m. p. 103°, the constitution of which is proved because its Me ether, m. p. 85—86°, gives 4-hydroxy-2-methoxybenzaldehyde on hydrolysis (contrast phloroglucinaldehyde). 3 : 4-Diacetoxy-acetophenone (improved prep. from the ω-Cl-derivative), O-benzoylphloroglucinaldehyde, and HCl in dry EtOAc give benzoyl-luteolinidin chloride, +H_2O, which on debenzoylation and acidification affords (I), +1·5H_2O (corresponding picrate, +0·5H_2O, decomp. above 210°). ω : 3 : 4-Triacetoxyacetophenone, β-resorcylaldehyde, and HCl in dry EtOAc give (II), +H_2O. The colour reactions of (I) and (II) in buffered solutions are recorded. Partial hydrolysis of cyanin yielded, with difficulty, the 5-monoglucoside, the colour reaction of which with Na_2CO_3 is not in agreement with the 3 : 5-dimonoside structure for cyanin, which is, however, considered correct.

XIII. The 5-glucoside (I) and 5-lactoside (II) of hirsutidin (malvidin 7-Me ether) have been synthesised. The latter, but not hirsutin (hirsutidin diglucoside), very readily gives a cryst. ψ-base. The prep. of 2-O-benzoyl-4-O-methylphloroglucinaldehyde, m. p. 109° (obtained only in small yield by diazomethane), is modified. 2 - O - Tetra - acetyl - β - glucosidyl - 4 - O - methylphloroglucinaldehyde (from 4 - O - methyl-phloroglucinaldehyde), m. p. 177°, ω - hydroxy - 4 - acetoxy-3 : 5-dimethoxyacetophenone, and HCl in dry EtOAc give 3-hydroxy-5-o-tetra-acetyl-β-glucosidoxy-4' - acetoxy - 7' : 3' : 5' - trimethoxyflavylium chloride, partly deacetylated, + ?H_2O, which on hydrolysis and acidification affords 5-β-glucosidylhirsutidin

chloride, +2·5H$_2$O. 4-*O*-Methylphloroglucinaldehyde, *O*-hepta-acetyl-α-lactosidyl bromide, and KOH in aq. COMe$_2$ at 5—10° afford 2-*O-hepta-acetyl-β-lactosidyl-4-O-methylphloroglucinaldehyde*, m. p. 164°, which with ω : 4-dihydroxy-3 : 5-dimethoxyacetophenone led to 3 : 4′-*dihydroxy*-5-*O-hepta-acetyl-β-lactosidoxy-7 : 3 : 5′-trimethoxyflavylium chloride*, isolated as *Ac*$_2$ derivative, +4·5H$_2$O, and 5-β-*lactosidylhirsutidin chloride*, +5H$_2$O (ψ-base, +6H$_2$O, decomp. 150—165° after darkening at 102°).

Many colour reactions are detailed for all the above flavylium compounds and their mutual relationship is discussed. R. S. CAHN.

Yellow colouring matter of Khapli wheat, *Triticum dicoccum*. J. A. ANDERSON and A. G. PERKIN (J.C.S., 1931, 2624—2625).—A small amount of a flavone-like colouring matter, termed *tricin*, C$_{15}$H$_8$O$_5$(OMe)$_2$, m. p. 288° (*Ac*$_2$, m. p. 211—'213°, and *Ac*$_3$, m. p. 251—254°, derivatives), has been isolated from the leaves. Tricin is demethylated to *tricetin*, decomp. slowly above 330° (*Ac*$_4$, m. p. 260—261°, and *Ac*$_5$, m. p. 244°, derivatives), which when fused with KOH at 200° gives phloroglucinol and an acid resembling gallic acid. Tricetin is not 5 : 7 : 3′ : 4′ : 5′-pentahydroxyflavone.

H. BURTON.

Diphenylene oxide monosulphonic acid and the corresponding sulphone. J. ZEHENTER (J. pr. Chem., 1931, [ii], **131**, 331—336).—2 : 2′-Dihydroxydiphenyl is converted by 0·5 mol. of 17—18% oleum at 180—190° into *diphenylene oxide sulphonic acid*, SO$_3$H·C$_6$H$_3$>O (I) +H$_2$O, m. p. 133—135°, and anhyd., m. p. 163—165° (*K* +H$_2$O and anhyd., *Na* +H$_2$O and anhyd., *Ca* +6·5H$_2$O and anhyd., and *Cu* +6H$_2$O and anhyd., salts) (separated by its solubility in H$_2$O), and *bisdiphenylene oxide sulphone*, SO$_2$(·C$_6$H$_3$>O)$_2$, m. p. 208—209°, together with a little diphenylene oxide. Further treatment of (I) with 20% oleum at 120° affords the disulphonic acid obtained by Hoffmeister (A., 1871, 123), isolated as its Ba salt, +H$_2$O and +4·5H$_2$O. J. W. BAKER.

Effect of unsaturated chromophores on pyronine dyes. I. B. B. DIKSHIT and J. D. TEWARI (J.C.S., 1931, 2511—2514).—*Aconiteins* (I) and *tricarballyleins* (*dihydroaconiteins*) (II) are prepared, usually by methods previously described (A., 1927, 969, 977 ; 1929, 1186), from aconitic and tricarballylic acids, respectively, and the following substances ; the m. p. quoted first in brackets is that of (I), the other that of (II) : PhOH [250° (decomp.) ; 220° (decomp.)] ; resorcinol [190° (decomp.) ; 207° (decomp.)] ; pyrocatechol [150° ; 180° (decomp.)] ; phloroglucinol [blackens at 195° ; 119°] ; *m*-diethylaminophenol [112° ; 140° (decomp.) (shrinks at 130°)] ; *m*-dimethylaminophenol [118° (decomp.) ; 138°] ; *m*-phenylenediamine (condensed at 150—160° in presence of dry HCl) [248° ; 198—200° (decomp.) (blackens at 190°)] ; *o*-cresol (195° (decomp.)] ; 168° (decomp.) ; *m*-cresol [126° (decomp.) ;
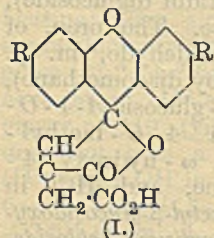
220° (decomp.)] ; pyrogallol [above 300° ; 236° (decomp.) (darkens at 195°)] ; tetrabromoresorcinol [decomp. above 170° ; 187° (decomp.) (darkens at 177°)] ; tetraiodoresorcinol [decomp. above 187° ; 215° (decomp.)]. The absorption maxima show that the aconiteins are more intensely coloured than their dihydro-derivatives.
H. BURTON.

Syntheses in the hydroaromatic series. O. DIELS and K. ALDER. XII, XIII. "Dien"-syntheses with heterocyclic oxygen compounds. 2. Furan [with H. NIENBURG and O. SCHMALBECK]. 3. Coumalin [with K. MÜLLER] (Annalen, 1931, **490**, 243—257, 257—266).—XII. (cf. A., 1929, 570). Furfuryl acetate and maleic anhydride in Et$_2$O give (after some days) 3 : 6-*endoxo-3-acetoxymethyl*-Δ^4-*tetrahydrophthalic anhydride*, m. p. 114°, reduced catalytically (Pd) in MeOH to a *compound*, C$_{12}$H$_{16}$O$_7$, m. p. 142—143°. Furan (I) and aq. maleic acid afford 3 : 6-*endoxo*-Δ^4-*tetrahydrophthalic acid* (+H$_2$O) (II), m. p. 103—105° (decomp.) (after sintering at 95°) with regeneration of (I), re-solidifying with m. p. 135°, best prepared by hydrolysis of its anhydride (*loc. cit.*). 4-*Bromo-5-hydroxy*-3 : 6-*endoxohexahydrophthalic acid* (III), m. p. 205°, from (II) and Br in H$_2$O, loses 1 mol. of H$_2$O when dried at 100°/high vac. over P$_2$O$_5$, and when treated with MeOH–HCl or Et$_2$O–diazomethane passes into the *bromolactonic* (cis-) *ester* (IV), m. p. 175°. Treatment of (IV) with HBr in AcOH at 100° gives a *bromolactonic acid* (as IV), m. p. 231—232°, which has a *trans*-configuration,
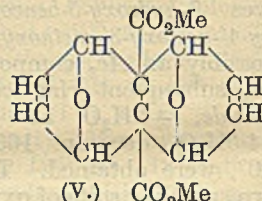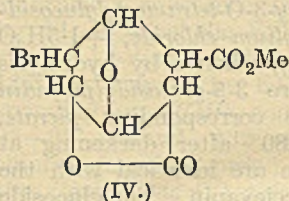
since it yields a *Me* ester, m. p. 167—168° ; similar treatment of (III) at 160—170° affords phthalic acid. Catalytic reduction (Pd–CaCO$_3$) of (III) in aq. EtOH–KOH and dehydration of the resultant product with AcCl gives the *lactonic acid* (IV, where CHBr=CH$_2$ and Me=H), m. p. 174—175°.

Me acetylenedicarboxylate and (I) at 100° afford a mixture of Me 3 : 6-endoxo-3 : 6-dihydrophthalate (not characterised) and *Me* 1 : 4 : 5 : 8-*diendoxo*-1 : 4 : 5 : 8 : 9 : 10-*hexahydronaphthalene*-9 : 10-*dicarboxylate* (V), m. p. 148° (decomp.) [free *acid* (VI), m. p. 158° (decomp.), formed from (I) and acetylenedicarboxylic acid]. Catalytic reduction (Pd) of the phthalate in COMe$_2$ gives *Me* 3 : 6-*endoxo*-Δ^1-*tetrahydrophthalate* (VII), m. p. 51—52° [free *acid* (VIII), m. p. 167—168° (decomp.)], oxidised by O$_3$ to oxalic and succinic acids. Phenyl azide and (VII) afford the *triazole* (IX), m. p. 162°, whilst (VII) and (VIII) are converted by
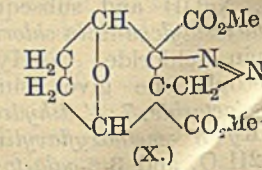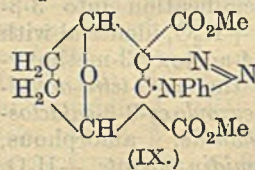

an excess of diazomethane in Et$_2$O into the *pyrazoline* (X), m. p. 112—113°.

Catalytic reduction (Pd) of (V) in MeOH yields *Me* 1 : 4 : 5 : 8-*diendoxodecahydronaphthalene*-9 : 10-*dicarboxylate*, m. p. 158—160° [free *acid*, m. p. 245—246°, obtained by reduction of (VI)], hydrolysed by EtOH–KOH to the *Me H* ester, m. p. 212°.
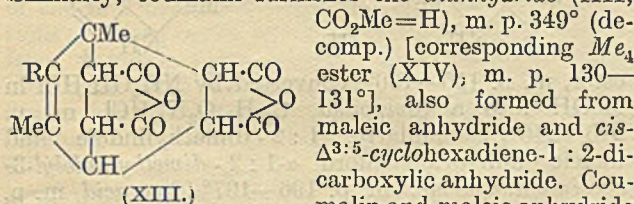
Me cis-3 : 6-*endoxohexahydrophthalate* (*norcantharidate*), m. p. 80—85°, prepared from the Me H ester (*loc. cit.*) and diazomethane, is converted by NaNH$_2$ in Et$_2$O into the Me ester of trans-*norcantharidic acid*, m. p. 179—180°

XIII. Me coumalate and maleic anhydride in boiling PhMe give about 30% of the *compound* (XI), m. p. 198°, converted by successive treatment with H$_2$O and MeOH–HCl into Me trimesate. When the reaction is carried out in boiling xylene, about 30% of the *compound* (XII), m. p. 331° (corresponding

(XI.)   (XII.)
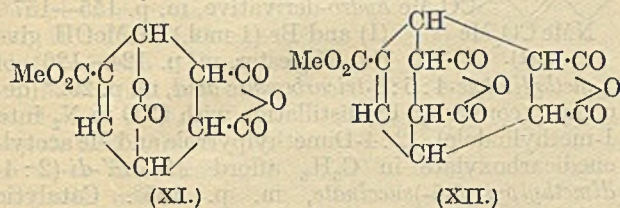
Me$_5$ ester, m. p. 137—138°), is formed after 24 hr., whilst (XI) results after 5 hr. (XI) is dehydrogenated by Br (2 mols.) at 200° to trimesic acid.

Dimethylcoumalin heated with maleic anhydride gives the *compound* (XIII, R=H), m. p. 274° (corresponding *Me$_4$* ester, m. p. 155°), whilst *iso*dehydracetic acid similarly affords the *compound* (XIII, R=CO$_2$H), m. p. 325° (corresponding *Me$_5$* ester, m. p. 204°). Similarly, coumalin furnishes the *dianhydride* (XII,

(XIII.)

CO$_2$Me=H), m. p. 349° (decomp.) [corresponding *Me$_4$* ester (XIV), m. p. 130—131°], also formed from maleic anhydride and cis-Δ$^{3:5}$-*cyclo*hexadiene-1 : 2-dicarboxylic anhydride. Coumalin and maleic anhydride in boiling PhMe give an *adduct*, C$_9$H$_6$O$_5$, m. p. 187°, which reacts further with maleic anhydride in boiling xylene yielding the above dianhydride. Catalytic reduction (Adams) of (XIV) in AcOH affords *Me* 3 : 6 - endo - αβ - *dicarbomethoxyethylenehexahydrophthalate*, m. p. 157°, convertible into the trans-modification, m. p. 112°, by the usual method.

H. BURTON.

Azopyrrole-blacks. III, IV. A. QUILICO and M. FRERI (Atti R. Accad. Lincei, 1931, [vi], **13**, 282—287, 377—382; cf. A., 1930, 793).—III. In glacial AcOH solution l-methylpyrrole readily reacts with diazotised (1) *p*-nitroaniline to give a black product, less intensely coloured and with a higher O content than that from pyrrole, and (2) 2 : 4-dinitroaniline to give a black product in lower yield and with 3—4% more C. In aq. solution made acid with AcOH, l-methylpyrrole and diazotised *p*-nitroaniline give 2-*p*-nitrobenzeneazo-1-methylpyrrole (cf. Ciusa, A., 1921, i, 365). 3-Methylpyrrole yields similar black products, but 2 : 4-dimethylpyrrole and diazotised *p*-nitroaniline in glacial AcOH give quantitatively 3-*p*-*nitrobenzeneazo*-2 : 4-*dimethylpyrrole*, m. p. 208°.

2-Methylpyrrole and diazotised *p*-nitroaniline yield (1) in dil. EtOH acidified with AcOH, 5-*p*-nitrobenzeneazo-2-methylpyrrole (?) and (2) in glacial AcOH, a brown oxidation or resinification product completely sol. in dil. alkali solution and containing less C and more N than the corresponding azopyrrole-black should do. T. H. POPE.

Cobalt nitrosodithiocarbamates. L. CAMBI and A. GAGNASSO [with A. TANARA] (Atti R. Accad. Lincei, 1931, [vi], **13**, 404—406).—The action of Co(OAc)$_2$ (1 mol.) on NH$_4$ or NH$_2$Me$_2$ dimethyldithiocarbamate (>2 mols.) in an atm. of NO at 0° yields *Co nitroso*-NN-*dimethyldithiocarbamate*, [(NMe$_2$·CS$_2$)$_2$Co·NO]. *Co nitroso*-N-*piperidyldithiocarbamate*, [(C$_5$H$_{10}$N·CS$_2$)$_2$Co·NO], is similarly obtained. Both are highly stable as crystals. T. H. POPE.

Reactivity of conjugated systems. IV. Condensation of alkylidene-ketones with cyanoacetamide. C. BARAT (J. Indian Chem. Soc., 1931, **8**, 699—710).—The activity of αβ-unsaturated ketones, CHR:CH·CO·R', towards cyanoacetamide is enhanced when R=alkyl as compared with R=aryl (A., 1930, 925); the difference is ascribed to the smaller vol. of the alkyl group. Michael condensation (*A*) of ethylideneacetophenone and cyanoacetamide gives mainly 3-*cyano*-2-*keto*-6-*phenyl*-4-*methyl*-2 : 3 : 4 : 5-*tetrahydropyridine* (I), m. p. 248—250°, and some 3-cyano-6-phenyl-4-methyl-2-pyridone [also formed by oxidation of (I) with HNO$_2$], whilst Knoevenagel condensation (*B*) affords 3-*cyano*-6-*hydroxy*-2-*keto*-6-*phenyl*-4-*methylpiperidine* (II), m. p. 177—178°, dehydrated by HCl in CCl$_4$ to (I). Hydrolysis of (I) or (II) with conc. HCl at 120—125° gives γ-*benzoyl*-β-*methylbutyric acid*, m. p. 72—73°, also obtained by heating γ-benzoyl-β-methylpropane-αα-dicarboxylic acid, m. p. 141—142° (decomp.), prepared from Et malonate and the above ketone. Similarly, ethylidene-*p*-methylacetophenone (*dibromide*, m. p. 120—121°) affords (*A*) 3-*cyano*-2-*keto*-6-*p-tolyl*-4-*methyl*-2 : 3 : 4 : 5-*tetrahydropyridine*, m. p. 255—256°, and (*B*) 3-*cyano*-6-*hydroxy*-2-*keto*-6-*p-tolyl*-4-*methylpiperidine*, m. p. 163—164°, both hydrolysed to γ-*p*-*toluoyl*-β-*methylbutyric acid*, m. p. 105—106°, also obtained from γ-*p*-toluoyl-β-methylpropane-αα-dicarboxylic acid, m. p. 125° (decomp.). Ethylideneacetone gives (*A*) 3-*cyano*-2-*keto*-4 : 6-*dimethyl*-2 : 3 : 4 : 5-*tetrahydropyridine*, sublimes when heated, and (*B*) 3-*cyano*-6-*hydroxy*-2-*keto*-4 : 6-*dimethylpiperidine*, m. p. 173—175°. Mesityl oxide condenses (*A* or *B*) with cyanoacetamide forming 3-*cyano*-6-*hydroxy*-2-*keto*-4:4:6-*trimethylpiperidine*, m. p. 273—275°, dehydrated to 3-*cyano*-2-*keto*-4 : 4 : 6-*trimethyl*-2 : 3 : 4 : 5-*tetrahydropyridine*, m. p. 252—254°, which is unaffected by HNO$_2$. *cyclo*Hexenyl Me ketone (III) gives (*A* or *B*) 4-*cyano*-3-*keto*-1-*methyl*-3 : 4 : 5 : 6 : 7 : 8 : 9 : 10-*octahydroisoquinoline*, m. p. 358—360° (N-*Me ether*, m. p. 122—123°), hydrolysed by 75% H$_2$SO$_4$ to 3 - *hydroxy*-1-*methyl* - 5 : 6 : 7 : 8 : 9 : 10 - *hexahydroisoquinoline*, m. p. 231—232° (decomp.), converted by successive distillation with Zn dust and PbO into l-methyl*iso*quinoline [*picrate*, m. p. 209—210°; *chloroplatinate*, m. p. 200—202° (decomp.)]. Hydrolysis of the product from (III) and Et malonate gives

1 : 3 - *dihydroxy* - 5 : 6 : 7 : 8 : 9 : 10 - *hexahydronaph - thalene*, m. p. 115°. H. BURTON.

Dihalides of pyridine. D. M. WILLIAMS (J.C.S., 1931, 2783—2787).—Pyridine dichloride, *dibromide* (I), m. p. 62—63°, *bromochloride*, m. p. 107—108°, iodochloride (II), and *iodobromide*, m. p. 116—117°, are prepared from pyridine and the requisite halogens in CCl$_4$; (II) is the most stable. The dissociation of (I) in CCl$_4$ is extremely small. Conductivity measurements with (II) in pyridine at 25° indicate the structure C$_5$H$_5$N·I·Cl; 2 of the valency electrons of the I atom are assumed to have entered the core. H. BURTON.

Action of ammonia on pyridine and 2-methyl-pyridine in presence of dehydrogenating catalysts. II. J. P. WIBAUT and L. M. F. VAN DE LANDE (Rec. trav. chim., 1931, 50, 1056—1059).—The yield of 2-aminopyridine obtained by the action of NH$_3$ on pyridine in presence of a Ni–Al$_2$O$_3$ catalyst (A., 1929, 1313) is decreased by carrying out the reaction at 320—360°/60—100 atm., the formation of 2 : 2'-dipyridyl being favoured under these conditions. With 2-methylpyridine and NH$_3$ in the presence of a Ni–asbestos catalyst at 430° a small yield of an *amino-2-methylpyridine*, b. p. 209—215° [*chloroplatinate*, m. p. 218—219° (decomp.); *picrate*, m. p. 203—204°], not identical with the 6-NH$_2$ compound, is formed. J. W. BAKER.

Biuret reaction. VI. Aminohydroxy-compounds which show the biuret reaction. M. TOMITA. **VII. Primary-quaternary bases which give the biuret reaction.** T. FUKAGAWA (Z. physiol. Chem., 1931, 201, 38—40, 40—46; cf. A., 1930, 585).—VI. Compounds containing the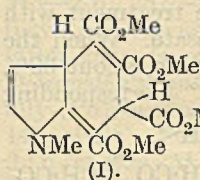 group ·CH(OH)·CH(NH$_2$)· give the biuret reaction. VII. γ - Chloro - β - hydroxypropylphthalimide (I) when heated with pyridine yields γ-*phthalimido-β-hydroxypropylpyridylium chloride* (II), m. p. 238—239° [*picrate*, m. p. 227—228°; *chloroplatinate*, m. p. about 218° (decomp.)]. (II) with moist Ag$_2$O forms the

betaine, C$_5$H$_5$:N·CH$_2$·CH(OH)·CH$_2$·NH·CO·C$_6$H$_4$·CO·O [open-chain *dipicrate*, m. p. 223—224° (decomp.)]. (II) when boiled with 20% HCl affords γ-*amino-β-hydroxypropylpyridylium chloride hydrochloride*, m. p. 229°, giving the biuret reaction. With quinoline at 130—140° (I) gives γ-*phthalimido-β-hydroxypropyl-quinolylium chloride*, m. p. 265—266° (*picrate*, m. p. 242°; *chloroplatinate*, m. p. 239°; *dipicrate* of betaine compound, m. p. 230°; γ-*amino-β-hydroxypropyl-quinolylium chloride hydrochloride*, m. p. 271—272°, gives no biuret reaction owing to decomp.). With *iso*quinoline at 130° (I) gives the corresponding *iso*quinolyl chloride, m. p. 255° (*picrate*, m. p. 197—198°; *chloroplatinate*, m. p. 227°; *dipicrate* of betaine compound, m. p. 192—193°; *hydrochloride* of NH$_2$-compound, m. p. 253, gives no biuret reaction owing to decomp.). J. H. BIRKINSHAW.

Syntheses in the hydroaromatic series. O. DIELS and K. ALDER. **XIV, XV. "Dien"-syntheses with heterocyclic nitrogen compounds. 2. Syntheses with pyrrole and acetylenedicarboxylic acid and its esters** [with H. WINCKLER]. **3. Indole** [with W. LÜBBERT and (in part) H. WINCK-

LER, E. HEINRICH, W. LÜCK, and W. ECKARDT] (Annalen, 1931, 490, 267—276, 277—294).—XIV. N-Methylpyrrole and acetylenedicarboxylic acid in Et$_2$O give α-N-*methylpyrryl-2-maleic acid*, m. p. 222—223° (decomp.), and (mainly) its *anhydride*, m. p. 164°. Catalytic reduction of the acid (as Na salt) affords α-N-*methylpyrryl-2-succinic acid* [*Me* ester, m. p. 72°, also formed by esterification of the acid obtained from the adduct (A., 1929, 819) from N-methylpyrrole and maleic anhydride]. Prolonged interaction of N-methylpyrrole and Me acetylenedicarboxylate (2 mols.) gives the *indole* (I), m. p. 145—148°, reduced in presence of (*a*) colloidal Pd and MeOH and (*b*) Pt-black and AcOH to (*a*) a *dihydro-*, m. p. 114—116°, and (*b*) the *hexa-hydro*-derivative, m. p. 155—157°. (I) and Br (1 mol.) in MeOH give the *Me$_3$ ester*, m. p. 124—126°, of 1-*methylindole*-4 : 5 : 6-*tricarboxylic acid*, m. p. 292° (decomp.) (converted by distillation with CaO in N$_2$ into 1-methylindole). 2 : 4-Dimethylpyrrole and Me acetylenedicarboxylate in C$_6$H$_6$ afford *Me αα'-di-*(2 : 4-*dimethylpyrryl*-5-)*succinate*, m. p. 165°. Catalytic reduction (Pd) of the adduct (this vol., 849) from 2-methylpyrrole and Me acetylenedicarboxylate gives Me α-2-methylpyrryl-5-succinate (*loc. cit.*).

XV. 2-Methylindole and maleic anhydride in C$_6$H$_6$ give α-2-*methylindolyl-3-succinic anhydride*, m. p. 169° [free *acid*, m. p. 212° (decomp.) (*Me* ester, m. p. 103°)], and the *compound* (II), m. p. 235—236° (*Me*
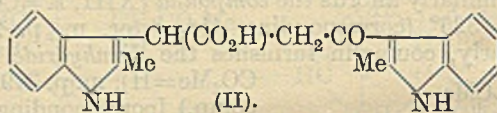
ester, m. p. 155—156°, converted by NH$_2$OH,HCl in MeOH into a *compound*, C$_{23}$H$_{24}$O$_3$N$_4$,HCl, m. p. 245—246°). Similarly, 1 : 2 - dimethylindole and maleic anhydride afford α-1 : 2 - *dimethylindolyl-3-succinic anhydride*, m. p. 196—197° {free *acid*, m. p. 233° [*Me* ester (III), m. p. 139°]}, and the *compound* (II, NH=NMe), m. p. 253°. *Me* 1 : 2-*dimethyl-indolyl-5-ethylene-αβ-dicarboxylate*, m. p. 129°, from 1 : 2-dimethylindole and Me acetylenedicarboxylate, is reduced catalytically (Pd) in MeOH to (III). Indole (or di-indole) and maleic anhydride in AcOEt give the *compound* (IV), m. p. 157° (*Me* ester, m. p, 151°), converted by an excess of diazomethane into a *substance*, C$_{22}$H$_{20}$O$_3$N$_4$, m. p. 172°. Catalytic reduction (Adams) of (IV) in MeOH furnishes a *dihydro*-derivative, m. p. 169—170° (prepared also from di-indole and succinic anhydride in AcOEt), hydrolysed by 30% KOH to indole and succinic acid. Similar hydrolysis of (IV) yields indole and
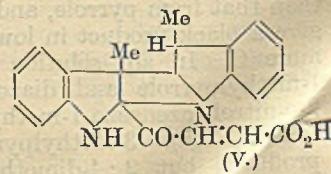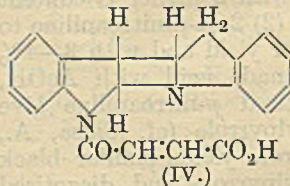
an *acid*, C$_{12}$H$_{11}$O$_4$N, m. p. 197° (*Me$_2$* ester, m. p. 74°). 3-Methylindole and maleic anhydride react

slowly in presence of a little conc. H_2SO_4, forming the *compound* (V), m. p. 246° [an *isomeride* (VI), m. p. 194°, is produced from di-3-methylindole and maleic anhydride in C_6H_6], hydrolysed to di-3-methylindole and fumaric acid, and converted by diazomethane into a *substance*, $C_{24}H_{24}O_3N_4$, m. p. 179°. Catalytic reduction (Pd) of (V) or (VI) gives the same *dihydro-*derivative (+EtOH), m. p. 207° (*Me* ester, m. p. 150°), also prepared from di-3-methylindole and succinic anhydride in AcOEt.   H. BURTON.

Polymerisation of indole. III. Polymerisation mechanism in hydrochloric acid solution. O. SCHMITZ-DUMONT and H. H. SAENGER (J. pr. Chem., 1931, [ii], **132**, 39—58; cf. this vol., 1165).—The reversibility of the polymerisation of indole into di-indole hydrochloride in aq. HCl is proved by the complete conversion of the latter by shaking with dil. HCl and Et_2O into indole. The lack of relationship between HCl concentration and the position of equilibrium is probably explained by the mechanism $C_8H_7N,HCl+C_8H_7N \rightleftharpoons (C_8H_7N)_2,HCl$. Addition of indole in EtOH to a mixture of conc. HCl and EtOH gives an immediate precipitation of di-indole hydrochloride, and no tri-indole is formed. Tri-indole is formed by combination of equiv. proportions of indole and di-indole hydrochloride (but not the base) at 100°, and also by careful neutralisation of a suspension of di-indole hydrochloride in H_2O with dil. KOH; it is the stable polymeride at room temp., and its formation is not reversible. Measurements are made of the solubilities of di- and tri-indole hydrochlorides in aq. HCl of varying concentration, and of di-indole hydrobromide in HBr. The solubility of the first decreases with increasing HCl concentrations; consequently the velocity of formation of tri- from di-indole hydrochloride, which increases with increasing HCl concentration at first, and then diminishes, is explained as a result of the opposing catalytic (due to p_H) and solubility effects. The formation of di-indole hydrobromide only with comparatively dil. HBr is a consequence of its even lower solubility in aq. HBr.   H. A. PIGGOTT.

Indole derivatives of mixed function. Q. MINGOIA (Gazzetta, 1931, **61**, 646—650; cf. A., 1929, 579).—In the prep. of 3-chloroacetylindole by the action of AcCl on magnesylindole, some *2-chloroacetylindole*, m. p. 230° (*Ag* derivative), is formed, giving when fused with KOH indole-2-carboxylic acid. Magnesylskatole with AcCl gives *2-chloroacetyl-3-methylindole*, m. p. 115—120°, converted by KOH into *2-chloroacetyl-3-methylindolylcarbinol*, m. p. 198—200° (*Ag* derivative; *Ac₂* derivative, m. p. 168°), and reacting with NH_3 in a sealed tube to give *2-amino-acetyl-3-methylindole*, m. p. 250—252° (decomp.) (*Ag* derivative; *picrate*, m. p. 170°). 3-*Aminoacetylindole*, m. p. 237° [*Ag* derivative; *picrate*, m. p. 200° (decomp.)], is similarly obtained from 3-chloroacetyl-indole.   E. E. J. MARLER.

Configurations of aldoximes. T. W. J. TAYLOR, D. H. G. WINCKLES, and M. S. MARKS (J.C.S., 1931, 2778—2783).—Quinoline-2-aldoxime (I) (A., 1903, i, 53) has a configuration (probably) similar to that of α-benzilmonoxime, since it furnishes a series of metallic (Co, Cu``, and Fe``) complexes. The regeneration of

(I) by hydrolysis of its *Ac* derivative, m. p. 128—130° (decomp.), with aq. Na_2CO_3 supports the view that when AcOH is eliminated from an acetylaldoxime (with nitrile formation), the H atom and OAc group are *anti* to one another. Metallic complexes are not obtained from the α-furfuraldoxime of Brady and Goldstein (A., 1927, 973), whilst the *Cu* and *Co* complexes from the β-form (*loc. cit.*) resemble those from β-benzaldoxime and are unlike those from α-benzilmonoxime (II).

β-Benzilmonoxime and $Cu(OAc)_2$ react slowly in EtOH forming a Cu complex which is decomposed by acid to (II); the production of a Co complex from the β-oxime is accelerated by ultra-violet light, indicating that the change β-oxime $\longrightarrow$ (II) occurs during these reactions.   H. BURTON.

Doebner's reaction. II. G. CARRARA (Gazzetta, 1931, **61**, 623—626; cf. A., 1928, 1024).—The mechanism of the reaction between benzylidene-aniline and pyruvic acid is discussed, and the hypothesis of Ciusa and Musajo (A., 1930, 222) is criticised.   E. E. J. MARLER.

Quinoline derivatives. XXXIII. 4-Amino-2-phenyl-6- and -8-methylquinoline. H. JOHN (J. pr. Chem., 1931, [ii], **132**, 15—23).—The following are described: 2-phenyl-6-methylquinoline-4-carboxylic acid [*chloride*, m. p. 199° (decomp.); β-*hydroxyethylamide*, m. p. 191°; *Me*, m. p. 85°, and β-*chloroethyl*, m. p. 81°, esters; *hydrazide*, m. p. 216° (*CHPh:*, m. p. 234°, and *CMePh:*, m. p. 227°, derivatives); *azide*, decomp. 210°]; 4-amino-2-phenyl-6-methylquinoline (from -4-carboxylic acid by means of azide and urethane) [*picrate*, m. p. 208°; *Ac₂*, m. p. 247°, N-CO_2Et (from azide), m. p. 178°, and NN'-*carbonyl* (from azide), m. p. 189°, derivatives]; 4-*carbimido-2-phenyl-6-methylquinoline*, m. p. 214° (decomp.); 1-(2'-*phenyl-6'-methyl-4'-quinolyl)-3-methyl-5-pyrazolone*, m. p. above 300°; 2-phenyl-8-methylquinoline-4-carboxylic acid [*chloride*, m. p. 245° (decomp.); *amide*, m. p. 241° (NN'-*carbonyl* derivative, m. p. 210°, from chloride and carbamide); *diethylamide*, m. p. 107°; β-*hydroxyethylamide*, m. p. 198°; *Me*, m. p. 86°, *Et*, m. p. 70°, and β-*chloroethyl*, m. p. 84°, esters; *hydrazide*, m. p. 222° (*CHPh:*, m. p. 226°, and *CMePh:*, m. p. 215°, derivatives); *azide*, decomp. 90°]; 4-*amino-2-phenyl-8-methylquinoline*, m. p. 125° [*Ac*, m. p. 212°, *Ac₂*, m. p. 293°, N-CO_2Et, m. p. 134° (from azide), and NN'-*carbonyl*, m. p. above 300° (from azide), derivatives]; 4-*carbimido-2-phenyl-8-methylquinoline*, m. p. 261° (decomp.); and 1-(2'-*phenyl-8'-methyl-4'-quinolyl)-3-methyl-5-pyrazolone*, m. p. above 300°.   H. A. PIGGOTT.

Constitution of the bases formed by the action of phosphoryl chloride on acetanilide and phenacetin. O. G. BACKEBERG (J.C.S., 1931, 2814—2817).—The products obtained by Silberstein (G.P. 137,121) from the action of PCl_5 on NHAcPh and phenacetin are shown to be, besides the corresponding substituted acetamidines, 4-anilino- (I), m. p. 156° (*hydrochloride*, m. p. 266°), and 4-p-*phenetidino-6-ethoxy-2-methylquinoline* (II), m. p. 225° (*hydrochloride*, m. p. 264°), respectively, the latter also being prepared from 4-chloro-6-ethoxyquinaldine and p-phenetidine. (I) when heated under pressure with fuming HCl

gives 4-hydroxy-2-methylquinoline and (II) similarly treated loses OEt-groups, but the $(OH)_2$-compound cannot be isolated. 4-Hydroxy-6-ethoxy-2-methyl-quinoline (hydrochloride, m. p. 241—243°) is converted by PCl_5 into 4-chloro-6-ethoxy-, m. p. 78°, and by fuming HCl into 4 : 6-dihydroxy-2-methylquinoline, $+H_2O$, m. p. 308° (decomp.). F. R. SHAW.

Manufacture of aminoalkoxy-compounds useful as antiseptics. Soc. CHEM. IND. IN BASLE.—See B., 1931, 1027.

Acridine. VII. Nitration of acridone. VIII. Nitration of 10-methylacridone and preparation of 3 : 7-diamino-10-methylacridinium chloride. K. LEHMSTEDT (Ber., 1931, 64, [B], 2381—2386, 2386—2394).—VII. Acridone, prepared by the action of NaOCl on thioacridone, is converted by HNO_3 (d 1·5) and AcOH in presence of conc. H_2SO_4 at $\not>30°$ into 3-nitro- (identified as 3-nitro-5-p-dimethyl-aminophenylacridine, m. p. 225°) and 1-nitro-acridone, m. p. 258—259°. Further nitration of 3-nitroacridone affords mainly 3 : 7-dinitroacridone [identical with the product of Bogert and others (A., 1930, 1047) ; 3 : 7-di-nitro-5-p-dimethylaminophenylacridine, decomp. 328° (corr.)] and a little 3 : 9(or 1 : 7)-dinitroacridone, m. p. 302°, also prepared by nitrating 1-nitroacridone. Acridone-1-carboxylic acid is nitrated to 7-nitro-acridone-1-carboxylic acid, decomp. 345°, decarboxyl-ated at 355° to 3-nitroacridine.

VIII. [With H. HUNDERTMARK.] Acridine is heated with Me_2SO_4 at 100° and the product after treatment with 2N-NaOH is oxidised with CrO_3 in AcOH, whereby 10-methylacridone, m. p. 199°, is obtained in good yield. Nitration in AcOH with HNO_3 (d 1·4) at 100° gives 3-nitro-10-methylacridone, m. p. 276° (also prepared from 3-nitroacridone, NaOMe, and MeI in EtOH), and 1-nitro-10-methyl-acridone, m. p. 168° (obtained also by methylation of the 1-NO_2-compound). 3 : 7-Dinitro-10-methyl-acridone, m. p. 350° (decomp.), is obtained from the 3-NO_2-compound, conc. H_2SO_4, and HNO_3 (d 1·4) or from 10-methylacridone, conc. H_2SO_4, and HNO_3 (d 1·51) (also from 3 : 7-dinitroacridone and Me_2SO_4). Reduction of 3-nitro-10-methylacridone by HCl and $SnCl_2$ affords 3-amino-10-methylacridone, m. p. 205°, transformed by 20% HCl at 220° into 3-hydroxy-10-methylacridone, m. p. 275° (decomp.), converted by NaOMe and Me_2SO_4 into 3-methoxy-10-methylacridone, m. p. 139° (picrate). Similarly 3 : 7-dinitro-10-methylacridone is reduced by Sn and HCl to 3 : 7-di-amino-10-methylacridone, m. p. 245—247° (hydro-chloride), which with Zn dust and conc. HCl yields 3 : 7-diamino-10-methyl-5 : 10-dihydroacridine, oxid-ised to 3 : 7-diamino-10-methylacridinium chloride, $C_{24}H_{14}N_3Cl,HCl,4H_2O$. H. WREN.

Determination of the constitution of bases obtained from protein. I. Isolation of sub-stituted piperazines and a new method for their synthesis. F. WREDE, E. BRUCH, and W. KEIL (Z. physiol. Chem., 1931, 200, 133—144).—Treatment of gliadin according to Troensegaard's method (this vol., 245) gave three bases isolated as the chloroaurates : 2-isopropylpiperazine (I) [chloroaurate (B,2HAuCl_4), darkens at 230°, decomp. 243° ; hydrochloride, m. p. 280° (darkens) ; picrate, decomp. about 250° ; chloro-

platinate ; Bz_2 derivative, m. p. 225° (uncorr.)] ; base, $C_5H_{11}ON$ (II) [chloroaurate (B,HAuCl_4), sinters at 164°, m. p. 174°], and 2-methylpiperazine (III) [chloroaurate (B,2HAuCl_4), darkens at 225°, decomp. 235° ; chloroplatinate, blackens at 270°, Bz_2 derivative, m. p. 150° (uncorr.)].

Electrolytic reduction of diketopiperazines under stated conditions gave piperazine and homologues ; 3 : 5-diketopiperazine gave piperazine, 3 : 5-diketo-2-methylpiperazine gave (III), and 3 : 5-diketo-2-isopropylpiperazine gave (I). The base (I) was previously isolated by Troensegaard (this vol., 1173).
J. H. BIRKINSHAW.

cycloDipeptides of asparagine. II. R. NUCCO-RINI and C. RAVENNA (Gazzetta, 1931, 61, 657—664 ; cf. A., 1930, 617).—The product obtained by heating asparagine in glycerol contains a small amount of the diamide of the α-cyclodipeptide of aspartic acid. Treatment of the remainder of the product with $Ba(OH)_2$ yields the β-dipeptide and a small amount (not rigorously identified) of the α-dipeptide of aspartic acid. It is suggested that in the original reaction there are formed (a) either the hypothetical β-cyclodipeptide, converted by $Ba(OH)_2$ into the β-dipeptide or its anhydride, which is known to give rise to the β-dipeptide (cf. A., 1922, i, 180), and (b) the diamide of the α-cyclodipeptide, by elimination of H_2O from the NH_2 and CO_2H groups of 2 mols. of asparagine, hydrolysis of this giving the α-cyclo-dipeptide, converted by $Ba(OH)_2$ into the α-dipeptide.
E. E. J. MARLER.

Racemisation. X. Action of alkali on di-ketopiperazines and peptides. P. A. LEVENE, R. E. STEIGER, and R. E. MARKER (J. Biol. Chem., 1931, 93, 605—621).—The anhydride of d-alanyl-d-alanine (I) is racemised to the extent of 80% by 0·2N-NaOH (2 mols.) at 25° during 48 hr. ; some hydrolysis occurs, but (I) is unaffected under the same conditions. Racemisation of d-leucyl-d-leucine anhydride by NaOH in aq. pyridine (cf. A., 1930, 788) is complete after 6 hr. Diketopiperazines are rapidly and completely racemised by alkali whenever hydrolysis does not occur. The figures quoted in parentheses after the following peptides (improved methods of prep. given) are the percentage racemis-ations taking place when they are treated (at 25°) with 0·2N- (2 mols.) and N-NaOH (10 mols.), re-spectively, after 8 days : d-leucyl-d-leucine (—, 0) ; d-leucyl-d-leucyl-d-leucine (0, 4) ; l-alanyl-d-leucyl-d-leucine (0, 5), $[\alpha]_D^{25}$ +62·2° in 1·01N-NaOH [prepared from l-α-bromopropionyl-d-leucyl-d-leucine, m p. 180° (decomp.), $[\alpha]_D^{25}$ +46·35° in EtOH]. H. BURTON.

Catalytic reduction of pyridine derivatives. Methyl- and phenyl-pyridine, quinoline, pyridyl-pyrrole, nicotyrine, and nicotine. J. OVERHOFF and J. P. WIBAUT (Rec. trav. chim., 1931, 50, 957—980).—Catalytic reduction (Adams) of these sub-stances under slight pressure at 40—50° in either AcOH or as their hydrochlorides in EtOH gives the following results. In agreement with Skita (A., 1916, i, 835), the velocity of reduction of pyridine, 2- and 3-, 2 : 4-di-, and 2 : 4 : 6-tri-methylpyridine to the corresponding piperidines decreases with increasing substitution. Quinoline (in EtOH) affords

cis- and trans-decahydroquinoline (A., 1927, 572). Only the pyridine ring is reduced in monosubstituted phenyl- or benzyl-pyridines, 2-phenyl-, 2- and 4-benzyl-pyridine giving the corresponding piperidines, whilst 4-phenylpyridine is not reduced. When more than one substituent Ph group is present, the Ph nucleus is also partly reduced or undergoes fission; 2 : 6-di-, 2 : 4 : 6-tri-, 2 : 3 : 5 : 6-tetra-, and penta-phenylpyridine give, respectively, 2 : 6-di(cyclohexyl)piperidine, m. p. 63°, 2 : 4 : 6-tri(cyclohexyl)-pyridine, m. p. 47°, a substance $C_{29}H_{39}N$, m. p. 224—225°, and a substance, $C_{29}H_{45}N$, m. p. 250—252°, probably a tetra(cyclohexyl)pyridine. N-2-Pyridylpyrrole undergoes fission into piperidine and pyrrolidine, but 2-(2′-pyridyl)pyrrole hydrochloride is reduced in EtOH to 2-(2′-piperidyl)pyrrole, m. p. 93° (benzenesulphonyl derivative, m. p. 125°), further reduced in AcOH to 2-(2′-piperidyl)pyrrolidine (picrate, m. p. 215°), whilst 3-(2′-pyridyl)pyrrole (only in EtOH) affords 3-(2′-piperidyl)pyrrole, m. p. 88—89° (hydrochloride, m. p. 207—208°). Reduction of nicotine causes fission of the pyrrole ring giving the octahydro-compound [3-δ-methylamino-n-butyl-piperidine (I)], which is the only product isolated, although in AcOH the large excess of H_2 absorbed indicates the occurrence of a side-reaction. Reduction of 2-(2′-pyridyl)- and 2-(3′-pyridyl)-N-methylpyrrole is effected only with carefully purified materials in AcOH, and whilst the former gives 2-(2′-piperidyl)-1-methylpyrrolidine, b. p. 225—228° (picrate, m. p. 189—190°), the latter gives only (I), fission of the reduced pyrrole nucleus taking place.

J. W. BAKER.

Quinazolines. II. Interaction of 2 : 4-dichloroquinazoline in alcohol with salts and bases. N. A. LANGE and F. E. SHEIBLEY (J. Amer. Chem. Soc., 1931, 53, 3867—3875).—The formation of 2-chloro-4-ethoxyquinazoline (I) from 2 : 4-dichloroquinazoline (II) and KCN in EtOH suggests that the reaction (II) + EtOH ⟶ (I) + HCl occurs; the HCl then reacts with the KCN. The possible replacement of KCN by other salts and bases is studied. (I) is formed from (II) and EtOH in presence of KCNO or Na_2CO_3, but with NaOAc a mixture of (I), AcOEt, benzoylenecarbamide [2 : 4-dihydroxyquinazoline] (III), and 2(?)-chloro-4(?)-hydroxyquinazoline, m. p. 211° [hydrolysed by dil. HCl to (III)], is obtained. (II) and NH_2Ph in EtOH give the hydrochloride, m. p. 317° (softens at about 304°), of 2 : 4-dianilinoquinazoline (not obtained free from EtOH except as a glass), m. p. 65° (indef.) [sulphate, m. p. 295°; acetate (+H_2O), m. p. 148°; nitrate, m. p. 223°; oxalate, m. p. 253°; picrate, m. p. 275° (softens at about 250°)]. o-, m-, and p-Aminobenzoic acids and (II) in EtOH afford the hydrochlorides, m. p. 271° (softens at 210°), 344°, and 347°, of 2 : 4-dianilinoquinazoline-2′ : 2″-, -3′ : 3″-, and -4′ : 4″-dicarboxylic acids (impure Cu salt), respectively. The hydrochloride of Me 2 : 4-dianilinoquinazoline-2′ : 2″-dicarboxylate melts partly at 181° (decomp.) after shrinking at about 160°, and completely at 261°. 4-Chloroquinazoline and NH_2Ph at 100° give the hydrochloride, m. p. 251°, of 4-anilinoquinazoline, m. p. 221—222° (picrate, m. p. 233°).

H. BURTON.

Disulphonic derivatives of 2-phenyl-αβ-naphth-1 : 2 : 3-triazole. A. NERI (Gazzetta, 1931, 61, 597—604).—The Na_2 salt of 2-p-sulpho-phenyl-3 : 4-naphth-1 : 2 : 3-triazole-1-sulphonic acid (I) is obtained by the action of NH_3–$CuSO_4$ on the Na_2 salt hexahydrate of p-sulphobenzeneazo-α-naphthyl-amine-4-sulphonic acid (from Na sulphanilate and Na naphthionate). (I) is oxidised by CrO_3 to the Na sulphonate of 2-phenyl-αβ-napthtriazolequinone already described (A., 1929, 1184). The Na_2 salt of 2-p-sulphophenyl-3 : 4-naphth-1 : 2 : 3-triazole-7-sulphonic acid (II) is similarly obtained from p-sulpho-benzeneazo-3-naphthylamine-7-sulphonic acid, prepared from sulphanilic acid and β-naphthylamine-6-sulphonic acid. Oxidation of (II) with CrO_3 gives unsatisfactory results. Treatment of 2-phenyl-αβ-naphth-1 : 2 : 3-triazole with excess of conc. H_2SO_4 gives a disulphonic acid (Ba salt +4H_2O; K_2 salt; Na_2 salt) not identical with (I) or (II). The free acid does not crystallise. Oxidation with CrO_3 gives small amounts of a quinone. E. E. J. MARLER.

Diethylaminoethyl ester of 2-phenyl-αβ-naphth-1 : 2 : 3-triazole-7′-carboxylic acid. A. NERI (Gazzetta, 1931, 61, 610—614).—Novocaine when diazotised and coupled with β-naphthylamine gives the hydrochloride of diethylaminoethyl p-azo-β-naphthyl-aminobenzoate (I) (non-cryst. base), converted by NH_3–$CuSO_4$ into diethylaminoethyl 2-phenyl-αβ-naphth-1 : 2 : 3-triazole-4′-carboxylate, (II), m. p. 162°, which does not form a hydrochloride.

(II.)

$N \cdot C_6H_4 \cdot CO_2 \cdot [CH_2]_2 \cdot NEt_2$
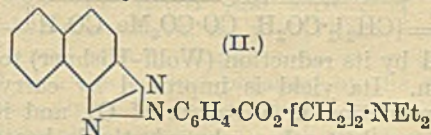
Similarly, the Na 4-sulphonate of (I) is prepared from novocaine and naphthionic acid, and yields the Na sulphonate of (II), which is not sufficiently sol. in H_2O for its physiological action to be tested.

E. E. J. MARLER.

Porphyrin syntheses. XL. Synthesis of deoxophylloerythrin. H. FISCHER and J. RIEDMAIR (Annalen, 1931, 490, 91—99).—Et 2-formyl-4-methyl-3-bromovinylpyrrole-5-carboxylate with cryptopyrrolecarboxylic acid in presence of HBr and AcOH gives 5-carbethoxy-4 : 3′ : 5′-trimethyl-3-bromovinyl-pyrromethene-4′-propionic acid hydrobromide, and with hæmopyrrolecarboxylic acid gives 5-carbethoxy-4 : 4′ : 5′-trimethyl-3-bromovinylpyrromethene-3′-propionic acid hydrobromide (I); the corresponding 5-carboxy-derivative [to (I)] (II) is similarly prepared. Fusion of (II) with 5-bromo-4 : 3′-dimethyl-3 : 4′-diethyl-5′-bromomethylpyrromethene hydrobromide and succinic acid gives mainly ætioporphyrin, deoxophylloerythrin (0.5% of theory), and an unidentified porphyrin, thus confirming the structure assigned to deoxophylloerythrin [cf. formula (II), this vol., 496]. A similar condensation could not be effected using (I) in the place of (II). H. A. PIGGOTT.

Chlorophyll. XVIII. Preparation and constitution of chlorophyll porphyrins. H. FISCHER, L. FILSER, W. HAGERT, and O. MOLDENHAUER. **XIX. Chlorophyll a.** H. FISCHER, O. SÜS, and G. CLEBS [with L. FILSER and H. SIEBEL] (Annalen,

1931, 490, 1—38, 38—90).—XVIII. Phylloerythrin, like chlorophyll, gives with MeOH–KOH in N_2 verdoporphyrin, accompanied by phyllo-, rhodo-, and pyrroporphyrins; in O_2 rhodoporphyrin-γ-carboxylic acid and chloroporphyrin e_5 are also formed. Phylloerythrin is formed by action of O_2 and AcOH on phæoporphyrin a_5, and is converted by further treatment with this reagent into rhodoporphyrin-γ-carboxylic acid by ring-fission at the CO·CH$_2$ linking. The similar behaviour of other chlorophyll derivatives, e.g., phæophytin (from which verdoporphyrin is formed in good yield with MeOH–KOH in N_2) and chloroporphyrin e_5, indicates the presence of the phylloerythrin structure. Phæophytin $a+b$, chlorophyllide $a+b$, phæophorbide a, and its Me ester all give phylloerythrin with 20% HCl in air or N_2, the formation of which in absence of air is probably accompanied by disproportionation. In absence of air phæophytin $a+b$ and phæophorbide a are degraded by MeOH–HCl to rhodoporphyrin Me$_2$ ester and chloroporphyrin e_4 ester. The intramol. migration of O that characterises many of these reactions explains the occurrence of *phæoporphyrin* a_7 (*mono*)*Me ester* [*Me$_3$* ester, m. p. 253° (decomp. into rhodoporphyrin and its Me$_2$ ester) (diazomethane or MeOH–HCl)] as the least sol. fraction of the reduction of phæophytin or phæophorbide a with HI in AcOH. Its constitution as rhodoporphyrin-γ-glyoxylic acid,
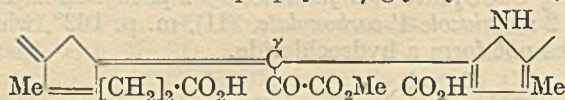
is proved by its reduction (Wolff–Kishner) to phylloporphyrin. Its yield is improved by carrying out the HI reduction in a stream of O_2, and it is the principal product when phæophytin is heated with AcOH in O_2 and the product reduced by addition of HI. When heated to 250° it gives rhodo- and, on longer heating, phyllo-porphyrin; it is also degraded to rhodoporphyrin by HBr–AcOH, MeOH–KOH at 155°, or by hot 95% HCO$_2$H or AcOH.

Chloroporphyrin e_5 gives pyrro- and rhodo-porphyrins with AcOH–air. Both phæophorbide a and methylphæophorbide a are decarboxylated by heating alone at 200°, or with pyridine at 160° (cf. A., 1930, 225); the products are reduced by HI to phylloerythrin and its ester. The conversion of phæoporphyrin a_5 into chloroporphyrin e_6 and phylloerythrin (this vol., 744) is also effected by HCl–Et$_2$O. A good yield of chloroporphyrin e_5 is obtained from e_6 by oxidation with air in AcOH. The *Fe* salt (hæmin ?) of phylloerythrin immediately gives the hæmochromogen spectrum with N$_2$H$_4$,H$_2$O, and is hydrolysed to phylloerythrin by dil. H$_2$SO$_4$ or HBr in AcOH. It is reduced by Na and amyl alcohol to deoxyphylloerythrin, traces of pyrro- and rhodo-porphyrins, and the *Fe* salt of decarboxylated chlorin e; similar treatment of natural chlorin e results in almost complete destruction. A product with all the properties of ψ-phylloerythrin is obtained by crystallisation of phylloerythrin with one tenth its weight of chloroporphyrin e_6 from pyridine–Et$_2$O. Phyllo- and ψ-phyllo-erythrin do not react with PhCHO or its p-NO$_2$-derivative in alkaline solution, but are converted into chloroporphyrin e_5. The action of Ag$_2$O

on chlorin e in pyridine gives an *Ag* derivative. The spectra of phylloerythrin and other porphyrins in Et$_2$C$_2$O$_4$ are described; in the case of the first-named combination with the solvent appears to occur.

XIX. The slightly modified formulæ (I or II) are proposed for chlorophyll and are discussed and compared with Conant's formula (cf. this vol., 744, 745;
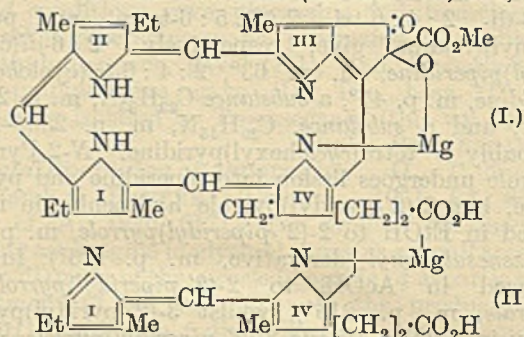
Conant, *ibid.*, 1075) in the light of allomerisation and the phase test. The action of KOH in PrOH on phæoporphyrin a_5 or of KOH in amyl alcohol on chloroporphyrin e, in both cases in air, leads to oxidation to a green chlorin-like *rhodoporphyrin-γ-carboxyanhydride* (III) [*Me* ester, m. p. 256° (diazomethane)], whereas in N_2 the former reaction results in simple hydrolysis to chloroporphyrin e_5. Energetic treatment with alkali converts (III) into rhodoporphyrin and its γ-carboxylic acid, and action of HI in AcOH on the Me ester gives rhodoporphyrin Me ester, and the propionic acid residue does not, therefore, take part in the anhydride formation in (III); either or both of the first two decomp. products are also obtained by use of conc. aq. HCl or of HBr in AcOH. The structure of (III) is confirmed by its formation by heating rhodoporphyrin-γ-carboxylic acid (IV) to 250°. The action of cold pyridine converts it into an unidentified porphyrin [*Me* ester, m. p. 250° (diazomethane)] spectroscopically intermediate between (IV) and phylloporphyrin. Oxidation of phæoporphyrin with H$_2$O$_2$ and H$_2$SO$_4$ gives (IV) with phæoporphyrin a_7 as by-product; the latter also gives (III) with KOPr and is regarded as an intermediate in the first method.

Me and Et chlorophyllides give phæoporphyrin a_5 exclusively on reduction with HI, whereas after allomerisation with O_2 or with air in MeOH they afford spectroscopic traces of phylloporphyrin with phæoporphyrin a_7 as main product, and some a_5. The chlorophyllides are unchanged by MeOH. Allomerisation of Et chlorophyllide with benzoquinone in EtOH in absence of air also occurs with absorption of 1 mol. O_2, but the product with HI gives *phæoporphyrin* a_6 [*Me* ester, m. p. 284° (*oxime*)], to which formula (V)
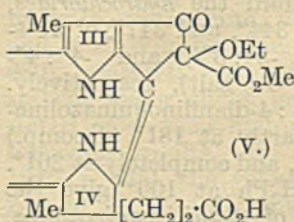
is assigned; this is decomposed by 10% KOH in MeOH to an unidentified porphyrin. It is therefore considered that whilst allomerisation with O_2 is a complex process which involves fission of the homocyclic nucleus, the product obtained with benzoquinone is a simple dehydro-derivative; this explains

the spectroscopic differences observed by Conant. Allomerisation with benzoquinone in EtOH is suppressed by traces of $H_2C_2O_4$, and reduction of the product obtained in $COMe_2$ gives phæoporphyrin a_5.

The phase test (cold KOH–MeOH) in presence of air gives with Et chlorophyllide the usual unstable chlorins which rapidly pass into a purpurin, and on reduction of the total product with HI rhodoporphyrin is formed; in N_2, however, chlorin e_7 (reduced by HI to chloroporphyrin e_5) and a little rhodin g are formed as in the hot quick hydrolysis. Using 25% KOH in PrOH under Conant's conditions a *purpurin*, $C_{33}H_{34}O_5N_4$ (*Me* ester, m. p. 254°), probably closely related to (III), results. Et chlorophyllide allomerised with benzoquinone in EtOH gives products converted by HI reduction into rhodoporphyrin whether the KOH hydrolysis is carried out in air or in its absence. It is concluded that the mechanism of the phase test consists in simple hydrolysis of the homocyclic ring. The change of the unstable chlorins into purpurins is reversible (*e.g.*, with phæopurpurin 7 Me_2 ester). Hydrolysis of chlorin e Me_3 ester with KOH–MeOH in N_2 gives chlorin e_7 and the purpurin previously obtained by hot, quick hydrolysis. Similar hydrolysis of phæophytin $a+b$ in N_2 gives a mixture of stable chlorins (e_6 and e_7), the latter of which is distinguished from the product obtained in air (phæopurpurin 7) by reduction with HI which gives chloro-e_6 and rhodoporphyrins, respectively. Degradation of dimethylphæopurpurin 7 with pyridine or "pyridine–soda" gives ψ-*verdoporphyrin* Me_2 ester, m. p. 277° (corr.), which with HI in AcOH gives rhodo-, and on energetic decomp. with alkali gives phyllo-porphyrin. The decarboxylation by heat of phæoporphyrin a_5 Me Et ester gives phylloerythrin Et ester.

H. A. PIGGOTT.

Action of fuming hydriodic acid on lupanine. K. WINTERFELD, A. KNEUER, and F. W. HOLSCHNEIDER (Ber., 1931, 64, [*B*], 2415—2419; cf. this vol., 371).—Treatment of *r*-lupanine in the manner adopted for *d*-lupanine affords β-lupinane and other non-identified products (cf. Clemo and others, this vol., 970). *d*-Lupanine hydrochloride is transformed by PCl_5 into *dichlorolupanine*, $C_{15}H_{22}ON_2Cl_2$, m. p. 112—113°, $[\alpha]_D$ +82.5° in 96% EtOH. d-*Lupanine H tartrate* has m. p. 194°.

H. WREN.

Cinchona **alkaloids. XXV. Complete synthesis of the** *Cinchona* **alkaloids, hydroquinine and hydroquinidine.** P. RABE, W. HUNTENBURG, A. SCHULTZE, and G. VOLGER (Ber., 1931, 64, [*B*], 2487—2500; cf. A., 1922, i, 360, 361).—Acetoacet-*p*-methoxyanilide, obtained from the ester and *p*-anisidine alone or in presence of solvent naphtha, is almost quantitatively converted by 90% H_2SO_4 at 100° into 2-*hydroxy*-6-*methoxy*-4-*methylquinoline*, m. p. 253° (*hydrochloride*), transformed by PCl_5 and $POCl_3$ at 115° into 2-*chloro*-6-*methoxy*-4-*methylquinoline*, m. p. 145° (corr.), which yields 6-methoxy-4-methylquinoline, m. p. 52°, when acted on by Al powder in 75% AcOH or by H_2 in presence of Pd and KOH–EtOH at 50—55°. Condensation of 6-methoxy-4-methylquinoline with boiling PhCHO in presence of anhyd. $ZnCl_2$ affords 6-*methoxy*-4-*styrylquinoline*, m. p. 75° (corr.) (*sulphate*), oxidised by $KMnO_4$ in aq. pyridine

to 6-methoxyquinoline-4-carboxylic acid (Et ester, m. p. 69°).

4-Methyl-3-ethylpyridine and CCl_3·CHO in presence of anhyd. $ZnCl_2$ at + 86° yield 3-ethyl-4-γ-trichloro-β-hydroxy-n-propylquinoline, m. p. 139° (corr.), transformed by NaOEt in 99.5% EtOH into 3-ethyl-pyridyl-4-acrylic acid, m. p. 248° (corr., decomp.) [*hydrochloride* +H_2O, m. p. 190° (corr., decomp.) after loss of H_2O at 110—120°]. The hydrochloride is reduced by H_2 in 4% aq. HCl in presence of highly active Pt sponge to a mixture of β-3-ethyl-4-piperidylpropionic acid hydrochlorides. The mixture of the corresponding Et β-3-ethyl-4-piperidylpropionates, b. p. 114—117°/0.3 mm., is treated with *d*-tartaric acid in anhyd. EtOH, whereby *Et* β-3-*ethyl*-4-*piperidylpropionate H* d-tartrate, m. p. indef. 123—124° (decomp.), $[\alpha]_D^{18}$ +6.6° in EtOH, is obtained; it is converted into Et β-3-ethyl-4-piperidylpropionate, b. p. 112—114°/0.1 mm., $[\alpha]_D^{18}$ +19.0° (*Bz* derivative, b. p. 197—200°/0.2—0.3 mm.), identical with the product obtained by alkaloidal degradation.

Condensation of the Bz derivative with Et quinate in presence of NaOEt affords hydroquinotoxin (I),
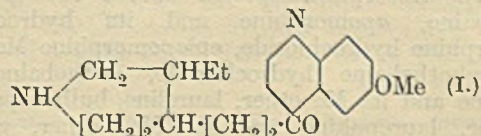
isolated as the Bz_2 d-tartrate, m. p. 170° (decomp.), $[\alpha]_D^{18}$ −39.5° in EtOH and $CHCl_3$ (1 : 2 vol.). N-*Bromohydroquinotoxin*, m. p. 117° after softening, is transformed into hydroquininone, m. p. 99—100°, identical with the product obtained by the oxidation of hydroquinine. Hydroquinotoxin is transformed into *C*-bromohydroquinotoxin dihydrobromide, and thence into hydroquininone. Hydrogenation of cryst. hydroquininone in presence of Pd yields hydroquinidine, whereas from the oily mixture of the ketonic and enolic forms of hydroquininone hydroquinine is obtained.

H. WREN.

Titration of quinine in ultra-violet light. J. GRANT (Analyst, 1931, 56, 653—654).—If quinine be dissolved in an excess of H_2SO_4 and the excess of acid titrated in a dark room under a vertical beam of ultra-violet light, free quinine is liberated at the end-point. This produces a marked decrease in the fluorescence, which, however, is not sharp unless carried out in presence of controls. The titration must be made in a beaker to avoid fluorescence due to the glass itself.

T. McLACHLAN.

Strychnos **alkaloids. LXII. Relationships of the C_{19} acids from brucidine and dihydrobrucidine.** H. LEUCHS, F. KRÖHNKE, and H. S. OVERBERG (Ber., 1931, 64, [*B*], 2539—2543; cf. this vol., 970).—Oxidation of dihydrobrucidine with CrO_3 yields, in addition to diketodihydronucidine (*loc. cit.*), minor amounts of an NH_2-acid, $C_{19}H_{24}O_4N_2$,$2H_2O$, m. p. 258—260° (decomp.), $[\alpha]_D^{20}$ +185.4°/*d* (*perchlorate*, $[\alpha]_D^{20}$ +141.1°/*d*), and an isomeric *acid* (+3H_2O), $[\alpha]_D$ +51.7°/*d*. Hydrogenation of either acid in presence of PtO_2 yields the *acid* $C_{19}H_{26}O_4N_2$, $[\alpha]_D$ +104.4°/*d* (*perchlorate*, $[\alpha]_D$ +74.9°/*d*), also obtained from the isomeric acids, $C_{19}H_{22}O_4N_2$, prepared by the oxid-

ation of brucidine (this vol., 855). The respective pairs must therefore be geometrical isomerides. Reduction of the acids $C_{19}H_{22}O_4N_2$ by Na–Hg is confined to the C:CH·CO$_2$H group and yields 2-keto-nucidine-3-acetic acid (isolated as the *perchlorate*, $C_{19}H_{24}O_4N_2,HClO_4$, $[\alpha]_D^{20}$ +50·3°/*d*), catalytically reduced to the acid $C_{19}H_{26}O_4N_2$. H. WREN.

Transposition of 2-benzeneazomorphine into 2-benzeneazoapomorphine. A. NEU (Gazzetta, 1931, **61**, 604—609; cf. A., 1930, 230).—2-Benzeneazomorphine dissolves in H$_2$SO$_4$ to give 2-benzeneazoapomorphine, identical with that obtained by the action of benzenediazonium chloride on *apo*morphine. 2-p-*Chlorobenzeneazomorphine* is similarly transformed into 2-p-*chlorobenzeneazoapomorphine*, identical with that obtained from *p*-chlorobenzenediazonium chloride and *apo*morphine. Neither Cl-compound melts below 300°. The structure of these compounds is discussed.

E. E. J. MARLER.

Absorption spectra of phenanthripyridine alkaloids. A. GIRARDET (J.C.S., 1931, 2630—2637).—Absorption spectra curves are given for thebaine, *apo*morphine and its hydrochloride, aporphine hydrochloride, epi*apo*morphine Me$_2$ ether, morphothebaine hydrochloride, *iso*thebaine, pukateine and its Me ether, laureline, bulbocapnine Me ether, laurepukine and its Me$_2$ ether, glaucine, dicentrine, domesticine Me ether, and corydaline. The effects of combinations of the substituents OH, OMe, :O$_2$CH$_2$, are discussed. H. BURTON.

Homologues of resorcinolarsinic acid and of 4-acetamido-2-hydroxyphenylarsinic acid (Fourneau 270). P. M. BARANGER (Bull. Soc. chim., 1931, [iv], **49**, 1213—1222).—The introduction of Me or Et *para* to the OH in *p*-amino- or *p*-acetamido-2-hydroxyphenylarsinic acid destroys the therapeutic val., the ratio maximum tolerated dose/curative dose decreasing to less than unity. A similar effect is observed with 2 : 4-dihydroxyphenylarsinic acid. The following are described : *p*-methoxyaceto-, b. p. 258°/160 mm., b. p. 146°/15 mm., m. p. 38—39° (yield 96%) (semicarbazone, m. p. 202°); *p-methoxypropio-*, b. p. 149—150°/19 mm., m. p. 20·5° (yield, 93%) (semicarbazone, m. p. 177°), *p*-methoxybutyro-, b. p. 158—159°/19 mm., m. p. 21—22° (yield, 91%) (semicarbazone, m. p. 183°), and p-*methoxyvalero-phenone*, b. p. 167°/25 mm. (80%) [semicarbazone, m. p. 220° (decomp.)]; *p*-heptoylanisole, b. p. 203°/25 mm. (yield 99%) (semicarbazone, m. p. 130°). Reduction of the above gives the alkylanisoles in the yield indicated; the latter are demethylated with gaseous HBr in boiling AcOH. *p*-Ethyl- (86%), b. p. 83—84°/16 mm., *p*-propyl- (70%) b. p. 107°/22 mm., *p*-butyl- (90%), b. p. 130°/33 mm., p-iso*amyl*- (56%), b. p. 121°/14 mm., p-*heptyl-anisole* (78%), b. p. 164°/23 mm.; *p*-ethyl- (93%), m. p. 45—46°, b. p. 217°, *p*-propyl- (90%), m. p. 20—21°, b. p. 120°/19 mm., *p*-butyl- (94%), m. p. 138—139°/18 mm., p-iso*amyl*- (80%), b. p. 126°/14 mm. and *p*-heptyl-phenol (87%), b. p. 176°/24 mm., m. p. 26°.

Nitration of the *p*-alkylphenols with dil. HNO$_3$ in C$_6$H$_6$ or AcOH at 0° affords the 2-nitro-4-alkylphenol, reduced to the 2-amino-4-alkylphenol with alkaline

Na$_2$S$_2$O$_4$. 3-Nitro-*p*-cresol (95%), m. p. 32°; 2-*nitro-4-propyl-* (72%), b. p. 124°/3 mm., -4-*butyl-* (71%), b. p. 125°/3·5 mm., -4-*heptyl-phenol* (87%), b. p. 149—150°/3 mm., m. p. 38°; 3-amino-*p*-cresol (85%), m. p. 135° [*Ac* derivative, m. p. 159—160° (decomp.)], 2-*amino-4-ethyl-* (100%), m. p. 137—138° (decomp.) [*Ac* derivative, m. p. 104—105° (decomp.)], -4-*propyl-* (100%), m. p. 143° (decomp.) [*Ac* derivative, m. p. 130° (decomp.)], -4-*butyl-* (100%), m. p. 138° (decomp.) [*Ac* derivative, m. p. 91—92° (decomp.)], and -4-*heptyl-phenol* (100%), m. p. 130° (decomp.) [*Ac* derivative, m. p. 112° (decomp.)], are thus obtained in the yield indicated and are converted into the 5-nitro-2-amino-4-alkylphenols by distillation and nitration of the *p*-ethenylphenols. 3-Ethenylamino-*p*-cresol (85%), b. p. 110—111°/18 mm., 2-*ethenylamino-4-ethyl-* (90%), b. p. 130°/25 mm., -4-*propyl-* (92%), b. p. 136°/18 mm., -4-*butyl-* (93%), b. p. 146—148°/18 mm., -4-*heptyl-phenol* (85%), b. p. 187°/18 mm., 6-*nitro-3-ethenylamino-p-cresol* (100%), m. p. 132°; 6-*nitro-3-amino-p-cresol* (70%), m. p. 199—200° (decomp.) [*Ac* derivative, m. p. 242°], 5-*nitro-2-ethenylamino-4-ethylphenol* (100%), m. p. 69°; 5-*nitro-2-amino-4-ethyl-* (100%), m. p. 155—156° (decomp.) (*Ac* derivative, m. p. 196°), -4-*propyl-*, m. p. 125—126° (decomp.) [*Ac* derivative, m. p. 160° (decomp.)], and -4-*heptyl-phenol*, m. p. 76° (decomp.); 5-*nitro-2-ethenylamino-4-propyl-*, an oil, and -4-*heptyl-phenol*, m. p. 119—120° (decomp.), are described.

4-*Nitro-2-hydroxy-5-methylphenylarsinic acid*, obtained from 6-nitro-3-amino-*p*-cresol by Bart's reaction (yield 30%), is reduced to 4-*amino-2-hydroxy* [*Na* salt; *Ac* derivative (*Na* salt)], converted into 2 : 4-*dihydroxy-5-methylphenylarsinic acid* (*Na* salt). 4-Nitro-2-hydroxy-, 4-*amino-2-hydroxy-* [*Na* salt; *Ac*-derivative (*Na* salt)], and 2 : 4-*dihydroxy-5-ethylphenylarsinic acid* (*Na* salt) are similarly obtained. The Bart reaction was unsuccessful when applied to the corresponding 4-propyl- and -heptyl-5-nitro-2-amino-phenols. R. BRIGHTMAN.

Aromatic arsenic compounds containing sulphur groups attached to the nucleus. III. 3 : 3′-Diamino-4 : 4′-dithiolarsenobenzene, the thiol analogue of salvarsan. H. J. BARBER (J.C.S., 1931, 2556—2561).—4-Chloro-3-nitrophenylarsinic acid and KSH in aq. EtOH give impure 3-*nitro-4-thiolphenylarsenic disulphide* (I), oxidised by HNO$_3$ (*d* 1·52) to 3-*nitro-4-sulphophenylarsinic acid* (II) and by I in presence of KI and NaHCO$_3$ to 2 : 2′-*dinitro-4 : 4′-diarsinodiphenyl disulphide* (III). Reduction of (I) with alkaline Na$_2$S$_2$O$_4$ gives 3 : 3′-*diamino-4 : 4′-dithiolarsenobenzene* (IV), whilst with Fe(OH)$_2$, 3 : 3′-*diamino-4 : 4′-diphenyldiarsenic trisulphide* results. The last-named is also reduced by Na$_2$S$_2$O$_4$ in presence of MgCl$_2$ to (IV). 3-Nitro-4-thiocyanophenylarsinic acid is oxidised by HNO$_3$ (*d* 1·52) to (II) and a little (III). H. BURTON.

10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. XVI. 10-Alkyl-5 : 10-dihydrophenarsazines as convenient sources of aliphatic dichloroarsines. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1931, 2518—2523).—Treatment of 10-chloro-5 : 10-dihydrophenarsazine with the appropriate Mg alkyl halide gives 10-Me, -Et-, -Pr-, -*Pr*$^\beta$-

m. p. 87—88°, -Bu-, m. p. 94—95°, -Bu^β-, m. p. 73—74°, -sec.-Bu-, m. p. 85—86°, -n-$amyl$-, m. p. 90—92°, and -α-$ethylpropyl$-, m. p. 110—111°, -5 : 10-dihydrophenarsazines. These are decomposed by dry HCl at 110—130° forming dichloroalkylarsines (65—85% yield); the following are prepared : $MeAsCl_2$, b. p. 132·5° (all b. p. are at 760 mm. except where stated otherwise), m. p. —42·5°; $EtAsCl_2$, b. p. 155·3°; $PrAsCl_2$, b. p. 175·3°, m. p. —28·2°; $Pr^\beta AsCl_2$, b. p. 168·6°; $BuAsCl_2$, b. p. 194·1°; $Bu^\beta AsCl_2$, b. p. 77·8°/20 mm; sec.-$BuAsCl_2$, b. p. 181·8°, and di-chloro-n-amylarsine, b. p. 212·9°, m. p. —45·5°. Mol. heats of vaporisation and Trouton's const. at 760 mm. are calc., and other physical data recorded, for these dichloroarsines. 2-Methyl-10-propyl-5 : 10-dihydrophenarsazine has m. p. 83·5—84·5°. H. BURTON.

Phenarsazine derivatives. I. P. G. SERGEEV and I. M. GORSKI (J. Gen. Chem. Russ., 1931, 1, 263—271).—Action of KCNS on 10-chloro-9 : 10-dihydrophenarsazine gives 10-thiocyano-9 : 10-dihydrophenarsazine, m. p. 229—230° (two forms). Boiling with xylene and treatment with NaOH and AcOH gives phenarsazinic acid. Diphenylthiocyanoarsine under the same conditions is unchanged, but with boiling H_2O gives diphenylarsine oxide. The acid is also obtained by heating phenarsazine cyanide or thiocyanate with tetralin. Phenarsazine chloride when heated with tetralin gives the hydrochloride of phenarsazinic acid. The following mechanism is suggested for the transformation of phenarsazine derivatives : $NH[C_6H_4]_2AsX \xrightarrow{O} NH[C_6H_4]_2As(O)X \xrightarrow{2H_2O} (NH[C_6H_4]_2As(OH)_2)X$. E. B. UVAROV.

Organo-chromium compounds and their relation to the complex chemistry of chromium. F. HEIN (J. pr. Chem., 1931, [ii], 132, 59—71).—A lecture. In a summary of partly unpublished researches it is shown that the Cr complexes that react with MgPhBr with formation of organo-chromium compounds are in general non-electrolytes. H. A. PIGGOTT.

Germanium. VII. Organic compounds of germanium. R. SCHWARZ and M. LEWINSOHN (Ber., 1931, 64, [B], 2352—2358).—Ge tetra-p-tolyl, m. p. 224°, prepared from $GeCl_4$ and Mg p-tolyl bromide in Et_2O, is converted by Br in $C_2H_4Br_2$ into Ge tri-p-tolyl bromide, m. p. 128°, and thence by PhBr and Na in xylene into Ge Ph tri-p-tolyl, m. p. 191°. The last-named compound with Br in boiling CCl_4 affords Ge Ph di-p-tolyl bromide, m. p. 119°, which with MgEtBr gives Ge Ph di-p-tolyl Et, b. p. 220°/13 mm., m. p. 55°, transformed by Br_2 in CCl_4 into Ge Ph p-tolyl Et bromide. Similarly, $GeCl_4$ and Mg p-diphenylyl bromide yield Ge tetra-p-diphenylyl, m. p. 270—272°, whence Ge tri-p-diphenylyl bromide, m. p. 242°, Ge tri-p-diphenylyl Et, m. p. 154—156°, non-homogeneous Ge di-p-diphenylyl Et bromide, and non-homogeneous Ge di-p-diphenylyl Et Pr^β. $GePh_4$ with twice its wt. of $GeCl_4$ at 210—290° affords Ge Ph trichloride, b. p. 105—106°/112 mm.; attempts to prepare the corresponding tribromide yield the di-bromide, b. p. 205—207°/12 mm., and (?) $Ge_2Ph_4Br_2$, m. p. 165°. $GePh_2Br_2$ and $MgPr^\beta Br$ give $GePh_2Pr^\beta Br$, b. p. 225—235°/13 mm., which yields $GePh_2EtPr^\beta$,

b. p. 175—190°, whence $GePhEtPr^\beta Br$, b. p. 130—135°/13 mm. Treatment of the last-named salt with Ag d-bromocamphorsulphonate in H_2O gives $GePhEtPr^\beta$ bromocamphorsulphonate, decomp. 230°, $[\alpha]_D^{20}$ +95·08° in H_2O. Ge tetra-p-tolyl and Br in CCl_4 afford Ge di-p-tolyl dibromide, b. p. 230—233°/13 mm. Excess of Na and $GePhCl_3$ in boiling xylene afford the compound $(GePh)_6$, possibly $GePh{\Large<}\begin{smallmatrix}GePh \cdot GePh\\GePh \cdot GePh\end{smallmatrix}{\Large>}GePh$. H. WREN.

Mercuration of higher aromatic hydrocarbons. I. M. GOSWAMI and H. N. DAS-GUPTA (J. Indian Chem. Soc., 1931, 8, 475—478).—The following compounds were prepared by heating the appropriate hydrocarbon and $Hg(OAc)_2$ in AcOH at 110—140°, filtering, concentrating, and adding $CaCl_2$ in AcOH : acenaphthene mercurichloride, m. p. 148° (decomp.), which with Ag_2O in boiling EtOH gives some mercurihydroxide, m. p. 184° after sintering at 175°; fluorene mercurichloride, m. p. 130—132° (decomp.), giving similarly the mercurihydroxide, m. p. 145—147°, in poor yield; anthracene mercurichloride, m. p. 181—183° (decomp.), decomposed by Ag_2O; phenanthrene mercurichloride, m. p. 155—157° (decomp.), decomposed by Ag_2O. The mercuri-hydroxides liberate NH_3 from NH_4Cl and absorb CO_2. The position of the Hg is unknown. R. S. CAHN.

Mercuric derivatives of dihydric bromophenols. M. AMADORI (Atti R. Accad. Lincei, 1931, [vi], 13, 371—374).—With dibromo-pyrocatechol and -resorcinol, $Hg(OAc)_2$ gives the compounds $C_6H_2O_2Br_2Hg$ and with the Br_3-derivatives, the compounds $C_6HO_2Br_3Hg$. T. H. POPE.

Mercury and halogen derivatives of 2-phenylcinchonic acid. M. DOMINIKIEWICZ (Rocz. Chem., 1931, 11, 664—669).—The following substances are described : 3-hydroxy- and -acetoxy-mercuri-2-phenylcinchonic acids, 3-iodo-2-phenyl- and 3-bromo-2-phenylcinchonic acids, m. p. 227—228° and 231°. The iododerivative yields o-iodobenzoic and 5-iodo-6-phenylpyridine-2 : 3 : 4-tricarboxylic acid on oxidation with $KMnO_4$. R. TRUSZKOWSKI.

Organic derivatives of silicon. XLV. Fission of aromatic Si–R linkings by aluminium chloride. W. E. EVISON and F. S. KIPPING (J.C.S., 1931, 2774—2778).—Treatment of a mixture of $SiPh_2Cl_2$ (1 mol.) and $AlCl_3$ (1 mol.) with EtBr (5 mols.) gives HBr, $SiCl_4$, $SiPhCl_3$, and Et derivatives of C_6H_6. $SiPh_2Cl_2$ and $AlCl_3$ react at 70° giving $SiCl_4$ and a solid (probably $AlPhCl_2$) which is converted by H_2O and AcCl into C_6H_6 and COPhMe, respectively; the reactions $SiPh_2Cl_2 + AlCl_3 = AlPhCl_2 + SiPhCl_3$; $SiPhCl_3 + AlCl_3 = SiCl_4 + AlPhCl_2$, probably occur. $SiCl_4$ is also produced when $SiPh_4$, $Si(CH_2Ph)_4$, or trianhydrotrisdiphenylsilicanediol is treated with $AlCl_3$ in $CHCl_3$, whilst octaphenylcyclosilicotetrane similarly gives a product, hydrolysed by H_2O to a solid (which probably contains some silico-oxalic acid). H. BURTON.

Tribenzylsilicane. W. E. EVISON and F. S. KIPPING (J.C.S., 1931, 2830—2831).—Tribenzylsilicane (I), m. p. 91°, has been isolated from a crude specimen of $Si(CH_2Ph)_4$ (A., 1928, 908). Tribenzyl-

silicyl oxide and H_2 are produced from (I), $COMe_2$, and KOH solution. H. BURTON.
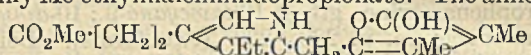
Aromatic tin compounds containing halogen in the nucleus. A. N. NESMEJANOV and K. A. KOTSCHESCHKOV (J. Gen. Chem. Russ., 1931, **1**, 219—232).—Such compounds are obtained by the reduction of org. Hg compounds by Sn^{II} salts (cf. this vol., 503). Compounds of the type $(XC_6H_4)_2SnX'_2$, where X, X' are halogens, so prepared are: *stannic di-p-chlorophenyl dichloride*, m. p. 86·5°, *dibromide*; *Sn di-p-bromophenyl dichloride*, m. p. 103°, *dibromide*, m. p. 82°; *Sn di-p-iodophenyl dichloride*, m. p. 147°, *dibromide*, m. p. 102°. The corresponding *di-iodides*, prepared by the action of NaI on the dichloride in hot EtOH, have m. p. 46—47° (X=Cl), 79—80° (X=Br), 88·5° (X=I). The action of alkali on these gives the corresponding *oxides* (infusible). H_2S in alkaline solution gives *sulphides* of the type $(XC_6H_4)_2SnS$, m. p. 179° (X= Cl), 228—229° (X=Br), 248° (X=I). Compounds of the type $XC_6H_4\cdot SnX'_3$ were obtained by heating the corresponding di-compound with Sn^{IV} halide in a sealed tube; *stannic p-chlorophenyl trichloride*, m. p. 39°, *p-bromophenyl trichloride*, m. p. 64·5—65°, *p-iodophenyl trichloride*, m. p. 55—56°, *p-iodophenyl tribromide*, m. p. 80—80·5°. Hydrolysis of the above trichlorides gives the corresponding infusible *acids*, $XC_6H_4\cdot SnOOH$. *Sulphides* of the type $(XC_6H_4Sn)_2S_3$ are obtained by the action of H_2S on acid aq. solutions of the trichlorides : m. p. 295° (decomp.) (X= Cl), 250° (decomp.) (X=Br), infusible (X=I). The action of Cl_2 in cold $CHCl_3$ on $(C_6H_4I)_2SnCl_2$ gives *stannic didichloroiododichloride*, m. p. 82—82·5°; and on $C_6H_4I\cdot SnCl_3$ gives *stannic dichloroiodotrichloride*, m. p. 50—70° (decomp.). E. B. UVAROV.

Action of acetic anhydride on amino-*tert.*-acids and dipeptides. Catalytic effects. Hydrolysis of *N*-acetyldipeptides. P. A. LEVENE and R. E. STEIGER (J. Biol. Chem., 1931, **93**, 581—604).—When pure α-amino*iso*butyric acid (I) is heated with Ac_2O at 150° (bath) a mixture of the corresponding azlactone and a *lactone* (II), $C_{10}H_{16}O_3N_2$ (alternative formulæ suggested), m. p. 143—144° (all m. p. are corr.) after slight previous sintering, is produced; if (I) contains traces of Cl and NH_3, the products formed are high-mol. solids. *dl-iso*Valine also gives some solid material in addition to azlactone, irrespective of the presence or absence of impurities. (II) is hydrolysed by H_2O at 25° to α-(α-*acetamido*isobutyryl)amino*iso*butyric acid (III), m. p. 223—225° (decomp.) [prepared by acetylation of α-(α-amino*iso*butyryl)amino*iso*butyric acid (IV), which is not hydrolysed by H_2O at 100°], and at 100° to an equimol. mixture of (I) and α-*acetamido*isobutyric acid, m. p. 195—196° after previous sintering; the same mixture is formed from (III) and H_2O at 100°. When (IV) is heated with AcOH α-amino*iso*butyric anhydride is produced; the rate of dehydration depends on the amount of impurity (NH_3). *dl*-α-Amino-α-phenylpropionic acid and Ac_2O at 150° give the azlactone (V) of *dl*-α-acetamido-α-phenylpropionic acid (VI), m. p. 202—203° (lit. 192—193·5°). (V) and aq. NH_3 afford dl-α-*acetamido-α-phenylpropionamide*, m. p. 191—192° after previous sintering, whilst (V) and (I) in AcOH yield α-(*dl - α - acetamido - α - phenylpropionamido*)iso-*butyric acid*, m. p. 214—215° (slight decomp.), readily hydrolysed by H_2O at 100° to (I) and (VI). Glycyl-α-amino*iso*butyric acid and Ac_2O in AcOH give α-(*acetamidoacetamido*)isobutyric *acid*, m. p. 190—191°, which is not readily hydrolysed by H_2O at 100°. H. BURTON.

Chromoproteins. I. Chromophoric group of the *Rhodymenia palmata*. P. A. LEVENE and A. SCHORMÜLLER (J. Biol. Chem., 1931, **93**, 571—579).—Peptic digestion of the seaweed followed by amyl alcohol extraction and Et_2O precipitation yields " phycobylin " (cf. A., 1928, 533; 1930, 488). Me-esterification gives a product resembling phycoerythrobilinic ester (cf. *ibid.*). The " phycobilin," however, contains 45% of the total N as NH_2-N and hence is termed " chromoproteinic acid." Reduction of this by HI yields a *substance*, $C_{17}H_{23}O_4N$, containing a little NH_2-N, whilst oxidation with CrO_3 yields mainly Me ethylmaleinimidopropionate. The annexed

$$CO_2Me\cdot[CH_2]_2\cdot C \underset{CEt\colon C\cdot CH_2\cdot C}{\overset{CH-NH}{<}} \underset{C\colon=CMe}{\overset{O\cdot C(OH)}{>}} CMe$$

structure is tentatively suggested for the phycoerythrobilinic ester. F. O. HOWITT.

Effect of alkali on protein. I. Optical behaviour of " racemic protein." F. A. CSONKA and M. J. HORN (J. Biol. Chem., 1931, **93**, 677—684).—Digestion of wheat gluten, caseinogen, and egg-albumin by 0·5N-NaOH at 38° yields optically-active products which with boiling 20% HCl lose their activity. This disagrees with Dakin's keto—enol theory of protein racemisation (A., 1913, i, 208). F. O. HOWITT.

Degradation of proteins. II. Colour reaction of glycine and other amino-acids with sodium hypochlorite and phenols. O. FÜRTH, A. FRIEDRICH, and R. SCHOLL (Biochem. Z., 1931, **240**, 50—61).—The blue colour obtained with glycine is very sensitive (down to 0·002%) but is not sp. It is given by other NH_2-acids and protein solutions, but much more faintly. The reaction is given very much more powerfully with NH_3 and NH_4 salts and the colour with NH_2-acids is due to the NH_3 liberated by hydrolysis, glycine being most easily hydrolysed. The pigment [using $(NH_4)_2CO_3$, NaOCl and PhOH] $C_{24}H_{17}O_6N_3Cl_4$ loses one third of its N in boiling alkali and gives with diazomethane a methoxy-methylimide derivative. P. W. CLUTTERBUCK.

Structure of proteins. IX. Degradation of caseinogen by warming with glycerol and the structure of the degradation products. A. FODOR and S. KUK. **X.** A. FODOR (Biochem. Z., 1931, **240**, 123—139, 140—148).—IX. Examination of various fractions is described and a double *tetrapeptide* is isolated, $C_{41}H_{67}O_{12}N_9,2H_2O$, possessing 2 free CO_2H and a free NH_2 group and formulated as prolylpyrrolidonyl-lysyl-leucine united to prolyl-pyrrolidonylalanyl-leucine through the two pyrrolidonyl groups.

X. A theoretical paper on the chemical structure of proteins based on the author's experiments on the ready dissociation of gelatin and caseinogen in glycerol into polypeptide components. P. W. CLUTTERBUCK.

Formation of biocolloids. I, II. S. J. VON PRZYLECKI and R. MAJMIN (Biochem. Z., 1931, 240, 98—122).—The extent of union of coagulated protein and starch varies with the p_H and is least at the isoelectric point. Ions which decrease the charge on the protein also decrease the amount of combined starch. Change of p_H does not, however, affect the amount of dextrin combined with protein. Reversibility of the union is not obtained on the acid side, but is obtained at the isoelectric point and above. Certain protein sols strongly decrease the amount of bound starch. When both components are employed as sols, the union of protein and starch and of protein and dextrin is readily detected in alcoholic solution at $p_H > 4.7$. In concentrations of EtOH in which separately the protein sol is stable whereas starch sol owing to its feeble charge is coagulated, in mixtures no coagulation occurs, the protein combining with the starch. Salts which decrease the charge on the protein also decrease its protective action.

P. W. CLUTTERBUCK.

[**Action of ammono-bases and sodium on**] **proteins in liquid ammonia. I.** E. W. McCHESNEY and C. O. MILLER (J. Amer. Chem. Soc., 1931, 53, 3888—3896).—Proteins are partly ammonolysed by ammono-bases in liquid NH_3, the extent depending on the base and temp.; H_2O-insol. proteins (fibrin, silk-fibroin) thereby become H_2O-sol. Treatment of silk-fibroin with Na in liquid NH_3 and esterification of the resultant product gives high-mol. products which yield cryst. picrates; methylation of the product with MeI in C_6H_6 affords an oil. Salt formation, ammonolysis, and reduction appear to occur when proteins are treated with Na in liquid NH_3. Glycyl-dl-alanine (Et ester $picrate$, m. p. 97—98°) and NHAcMe are practically unaffected by Na in liquid NH_3, whilst 2 : 5-diketopiperazine and Et aminoacetate are converted partly into bases.

H. BURTON.

Myosalvarsan, a reagent for protein and for testing colloid stability. W. MILBRADT (Z. physiol. Chem., 1931, 200, 166—168).—Myosalvarsan is a sensitive precipitant for proteins in presence of weak acid. The ppts. are dissolved by oxidising and reducing substances. It is proposed to use myosalvarsan as a reagent for quant. measurements of protein stability and as a qual. test for protein in urine.

J. H. BIRKINSHAW.

Determination of residual nitrogen by direct Nesslerisation. A. LUBLIN (Z. physiol. Chem., 1931, 201, 1—8).—Folin's method (A., 1919, ii, 308) is modified (a) by the use of $CCl_3 \cdot CO_2H$ instead of Na tungstate for precipitation of proteins, (b) by the use of H_2O_2 instead of $CuSO_4$ in ashing. In this way clouding during Nesslerisation is avoided. A standard carbamide solution is similarly treated.

J. H. BIRKINSHAW.

Analysis of gaseous hydrocarbons. R. ROSEN and A. E. ROBERTSON (Ind. Eng. Chem. [Anal.], 1931, 3, 284—289).—An apparatus for the prep. of synthetic mixtures of C_2H_6, C_3H_8, and butane, and the distillation of the condensed mixtures at 760 mm., is described. Graphs are constructed connecting distillation data and composition, and used for the determination of the above gases in stabiliser gases; when the last-named contain C_3H_6, a correction (curve given) is made for the butane content. The method compares favourably with that of Podbielniak (B., 1929, 799).

H. BURTON.

Analysis of three hydrocarbons by combustion. K. A. KOBE (Ind. Eng. Chem. [Anal.], 1931, 3, 262—264).—Equations are developed for use in conjunction with the method employed (cf. this vol. 457) for the determination of mixtures of H_2, CO, and CH_4. The method is applicable to hydrocarbons, H_2, CO, CO_2, O_2, CH_2O, and Me_2O.

H. BURTON.

Analysis of organic compounds by chromic acid. R. KUHN and F. L'ORSA (Z. angew. Chem., 1931, 44, 847—853).—Experimental details are given for the determination of C and H alone, or with certain combinations of the following groups : Ac, OEt, OMe, Me·C, by oxidation with CrO_3 to AcOH and CO_2; the necessary calculations are described and examples given.

R. S. CAHN.

Determination of halogens in organic compounds. M. B. SHCHIGOL (Farm. Zhur., 1929, 509—513).—The compound is reduced by Zn and AcOH in presence of NaOAc and $CuSO_4$, first in the cold for 1 hr. and then under a reflux condenser for 5—10 min. The halide is determined volumetrically.

CHEMICAL ABSTRACTS.

Determination of halogens in organic compounds using sodium sulphide. A. E. KRETOV, A. N. PANTSCHENKO, and K. K. SAVITSCH (J. Gen. Chem. Russ., 1931, 1, 419—422).—0.2 g. of substance is dissolved in 5 c.c. of EtOH, 7—8 c.c. of a solution containing 0.5—0.6 g. of $Na_2S,9H_2O$ in EtOH are added, and the mixture is heated for 30 min. under reflux at 100°, cooled, diluted with H_2O to 100 c.c., feebly acidified, and boiled until all the EtOH is expelled. Residual H_2S is oxidised by adding 3 c.c. of 30% H_2O_2 to the alkaline solution, which is then boiled a few min. to destroy excess of H_2O_2, and ionic halide is determined by Volhard's method. When coloured solutions are obtained after the action of H_2O_2, they should be further oxidised by $KMnO_4$ to the disappearance of the coloration. The above method is applicable to halogens present in aliphatic but not aromatic groups; when they are present in both the nucleus and the side-chain of aralkyl compounds only those of the side-chain are determined.

R. TRUSZKOWSKI.

Determination of nitrogen in nitro- and azo-compounds by the Kjeldahl method. B. G. ŠIMEK (Chem. Listy, 1931, 25, 322—325).—Azo- and NO_2-compounds are first reduced by boiling for 30 min. with alkaline-alcoholic $Na_2S_2O_4$, and then treated as usual with conc. H_2SO_4.

R. TRUSZKOWSKI.

Analysis of volatile compounds containing carbon, hydrogen, and nitrogen. W. SCHOLL and R. O. E. DAVIS (Ind. Eng. Chem. [Anal.], 1931, 3, 276—278).—An apparatus for the combustion of volatile org. compounds, and subsequent analysis of the mixture of CO_2, N_2 and H_2O vapour produced, is described. All reagents are used in the solid form.

H. BURTON.

Determination of sulphur in organic substances by means of the calorimetric bomb. II. F. GARELLI and B. SALADINI (Annali Chim. Appl., 1931, 21, 443—446; cf. B., 1931, 661).—Addition of a combustible liquid to the material renders possible the complete combustion of substances of low calorific power and tardy combustibility, such as thiocarbamide, "saccharin," etc., and also of explosive substances like picryl chloride which alone do not undergo combustion. S (0·1 g.) is burnt entirely to SO_3 if 0·5 c.c. of PhMe or decahydronaphthalene is added to it. T. H. POPE.

Determination of sodium in organic compounds. Use of uranyl acetate-[magnesium acetate] method. D. L. TABERN and E. F. SHELBERG (Ind. Eng. Chem. [Anal.], 1931, 3, 278—279).—Na barbiturates can be analysed (for Na) either electrometrically or by Kahane's method (A., 1930, 726), but not (generally) by conversion into Na_2SO_4. Kahane's method is applicable to Na salts of other org. acids. H. BURTON.

Modification of Pregl's micro-methoxyl apparatus. D. R. RIGAKOS (J. Amer. Chem. Soc., 1931, 53, 3903—3904).—Illustrations of 2 modifications are given. H. BURTON.

Determination of phenols in aqueous solution. Adaptation of bromine method to include range of 1—75 parts per million. J. A. SHAW (Ind. Eng. Chem. [Anal.], 1931, 3, 273—274).—The dil. aq. solution is acidified with H_2SO_4, the phenol extracted with Et_2O, and then removed from the extract with 10% NaOH. The alkaline solution is then acidified and analysed as described previously (B., 1929, 771). H. BURTON.

Gravimetric determination of phenol and salicylic acid by Lautemann's Red. M. FRANÇOIS and (MLLE.) L. SEGUIN (Bull. Soc. chim., 1931, [iv], 49, 1222—1229).—PhOH, salicylic acid, and Na salicylate are determined by dissolving 0·2 g. in 5 c.c. of NaOH (d 1·33), and 100 c.c. of H_2O and adding at 95° 1 c.c. at a time of N-I solution in KI, until a brown coloration persists. After boiling and cooling, excess of I is removed with Na_2SO_3 and the Lautemann's Red, $C_{12}H_4O_2I_4$, formed from 2 mols. of PhOH, is collected on a double 11-cm. filter, dried at 100°, and weighed. Bi salicylate is similarly determined after decantation from $Bi(OH)_3$. Salicylic acid in aspirin, salol, and Me salicylate are similarly determined, the ester being first hydrolysed by the NaOH. Determination of phenolphthalein by this method gave unsatisfactory results. R. BRIGHTMAN.

Argentometric determination of aldehydes. W. PONNDORF (Ber., 1931, 64, [B], 1913—1923).—MeCHO may be determined by oxidation with precipitated Ag_2O, the change being accelerated by heating the mixture and addition of alkali hydroxide when the concentration of aldehyde has become small. Unused Ag_2O is titrated with KI and unused Ag_2O dissolved in H_2SO_4 is determined in presence of starch iodide (this vol., 1259). Uniformity in operation is difficult to secure and the process is not applicable to slowly-reducing aldehydes (PhCHO) or to MeCHO in small amount. In a second method Ag_2O is precipitated simultaneously with $Mg(OH)_2$. With 5—45 mg. of MeCHO the enlargement of the active surface permits the determination to be effected at room temp. and with only slight alkalisation. CH_2O is similarly determined, but an experimental factor is required for dextrose. For more slowly reducing aldehydes (EtCHO or PhCHO) the reaction is accelerated by using a larger proportion of Ag_2O and more alkali hydroxide. In the case of 0·1—0·4 mg. of MeCHO, colloidal Ag_2O is used, prepared by adding NaOH to a solution of $AgNO_3$, $Al_2(SO_4)_3$, and Na_2SiO_3. For smaller amounts, retardation of the change is avoided by using SiO_2 as protective colloid; determination is effected in the absence of light. The colloidal condition of the Ag produced permits its direct titration with I and the intense colour of the solution renders a very rapid colorimetric or volumetric process applicable. H. WREN.

Determination of organic acids. III. Use of the isoamyl ether–water system in the partition method. IV. Provisional identification and determination of two fatty acids in a mixture. C. H. WERKMAN (Iowa State Coll. J. Sci., 1930, 5, 1—3, 121—125).—isoAmyl ether is preferred to Et_2O or Pr^β_2O on account of its smaller solubility in H_2O. Data are given for the pairs : acetic–propionic, –butyric, –lactic; propionic–butyric and –lactic acids. When the partition coeff. for Et_2O-H_2O indicates either of two binary mixtures, coeffs. using Pr^β_2O and isoamyl ether are determined. CHEMICAL ABSTRACTS.

Determination of salicylic acid in the presence of mineral acids (sulphuric and hydrochloric), and the simultaneous determination of all these acids together. O. A. KULSKAJA (Ukrain. Chem. J., 1931, 6, [Sci.], 1—8).—Seubert's method (A., 1882, 106) for the determination of PhOH gives good results (mean error 0·3%) for the determination of salicylic acid, in the presence or absence of HCl or H_2SO_4. HCl is determined by Volhard's method, and total acidity by titration against NaOH, the H_2SO_4 content being calc. by difference. R. TRUSZKOWSKI.

Colour reaction of adrenaline and adrenalone. M. PAGET (Bull. Sci. pharmacol., 1930, 37, 537—538; Chem. Zentr., 1931, i, 3136).—Adrenaline hydrochloride solution (2—3 c.c., 0·5%) with aq. NH_4 molybdate (1 c.c., 10%) gives a reddish-brown coloration which on addition of 6—7 drops of NaOH solution becomes green and fluorescent. 0·1% adrenaline solution gives an amber-yellow colour, changing with NaOH to green. 0·5% adrenalone solution gives with 1 drop of molybdate solution a yellow ppt., becoming orange on further addition of the reagent and then dissolving to a dichromate-coloured liquid which gives no green fluorescence with NaOH. 0·1% adrenalone solution gives a canary-yellow colour which is unchanged by NaOH. A. A. ELDRIDGE.

Alkaloidal reagents. I. Introduction. J. C. MUNCH, F. C. CROSSLEY, and W. H. HARTUNG (J. Amer. Pharm. Assoc., 1931, 20, 1037—1041).—As a preliminary to a systematic study of alkaloidal reactions, standard methods of prep. of alkaloidal

reagents and test solutions and a standardised procedure of testing have been developed.

E. H. SHARPLES.

Sensitivity of alkaloid reagents. I. SANSONI (Ind. Chim., 1931, **6**, 149—153; Chem. Zentr., 1931, i, 2907).—The sensitivity is increased by causing reaction to take place at the interface of two liquids and using a light or dark background.

A. A. ELDRIDGE.

Silicotungstates and double mercuric iodides of the amine-oxides of alkaloids : use in the determination of these bases. M. POLONOVSKI, M. POLONOVSKI, and J. CAPPELAERE (J. Pharm. Chim., 1931, [viii], **14**, 328—337).—The silicotungstates of vegetable alkaloids and alkaloidal amineoxides, with the exception of eserine, have the general composition $SiO_2,12WO_3,2H_2O,4$alkaloid,nH_2O. The eserine compound contains only 2 mols. of alkaloid. On ignition a residue of $SiO_2,12WO_3$ is left. Eserine and its amine-oxide both form $(HgI_2)_3,(alkaloid,HI)_2$. The quantity of eserine and its amine-oxide may be determined therefore in a mixture of the two. The m. p. of the silicotungstates of various alkaloids (and their amine-oxides) are : eserine, 197—198° (244°); strychnine 310° (310°); atropine 195° (187°); hyoscyamine 215° (212°); scopolamine 202° (decomp.) (chars about 200°); morphine, above 300° (above 300°). The silicotungstates are precipitated from a boiling solution in presence of a little HCl. The HgI_2 compounds are determined by precipitation,

washing with 5% H_2SO_4, and dissolving in a little HNO_3–H_2SO_4 (1 : 2). Excess of H_2O is added, followed by $0.1N$-$KMnO_4$ until a permanent colour is obtained, 10 drops of 10% Na nitroprusside are added, and the whole is titrated with $0.1N$-NaCl until the cloudiness disappears. T. McLACHLAN.

Biuret reaction of proteins. L. SCHULHOF (Magyar Chem. Fol., 1931, **37**, 10—16, 32—40, 50—55; Chem. Zentr., 1931, i, 2645—2646).—Cu complexes of biuret, gelatin, casein, gliadin, Witte's peptone, ovalbumin, serum-albumin, and serum-globulin were examined spectrophotometrically. In the visible spectrum the extinction coeffs. are of the same order of magnitude, but otherwise show marked differences. The extinction coeff. of proteins half- or quarter-saturated with $Cu(OH)_2$ did not give homologous vals.; hence the biuret reaction gives different complexes. The equiv. wts. of the various proteins with respect to $Cu(OH)_2$ show marked differences.

A. A. ELDRIDGE.

Determination of tryptophan and tyrosine. G. A. DA SILVA (Biochem. J., 1931, **25**, 1634—1640).—Any cystine which may escape decomp. by alkaline hydrolysis interferes with the determination of tyrosine. Histidine is precipitated with tryptophan by $HgSO_4$. The error can be obviated by determining total N and NH_2-N at the same time as the colorimetric or bromination determinations are made.

S. S. ZILVA.

Biochemistry.

Inhalation, retention, and exhalation of dusts and fumes by man. II. **Concentrations below 50 mg. per cubic metre.** C. E. BROWN (J. Ind. Hygiene, 1931, **13**, 285—291).—The retention of marble dust and MgO varies from 45 to 60% during normal breathing at rest with a concentration of 50—10 mg., but approaches 100% below 10 mg. per cu. m. Retention is decreased by 10% on inhalation of air containing 5% of CO_2.

P. G. MARSHALL.

Respiration, and function of hæmoglobin in *Planorbis corneus* **and** *Arenicola marina.* M. A. BORDEN (J. Marine Biol. Assoc., 1931, **17**, 709—738).—The blood-vol., O_2 consumption, combined and total blood-O, and O_2 capacity of the blood have been determined for these marine animals. Experiments are described which show that, during anaërobiosis, *Planorbis* goes into debt for O_2, whilst only partial debt is observed in *Arenicola*. Hæmoglobin functions as a transporter of O_2 for the former, and for the latter during low O_2 pressure.

A. COHEN.

Determination of minute volumes by the acetylene method during work by normal and diseased men. A. GROLLMAN, S. PROGER, and H. DENNIG (Arch. exp. Path. Pharm., 1931, **162**, 463—471).—The C_2H_2 method for determining the rate of circulation of the blood has been examined and adapted for more general application.

W. O. KERMACK.

Rôle of certain dietary factors in the formation of erythrocytes. B. C. GUHA and L. W. MAPSON (Biochem. J., 1931, **25**, 1674—1686).—There is a diminished red-cell count in rats suffering from vitamin-B_2-, but not from -B_1-deficiency. Autoclaved marmite, but not Cu, glutamic acid, extra Fe, or alkaline hæmatin, raises the blood count produced by this deficiency. An aq. extract of ox-liver after having the vitamin-B_2 activity destroyed by autoclaving in alkaline medium exerts a powerful influence on the formation of erythrocytes in rats suffering from vitamin-B_2 deficiency. S. S. ZILVA.

Acid-denaturation of hæmoglobin. N. U. MELDRUM (Biochem. J., 1931, **25**, 1498—1512).—Acid methæmoglobin exists at p_H vals. at which the protein is entirely precipitable. Curves are given for the amount of sol. native protein obtained from methæmoglobin solutions brought to different p_H. Acid methæmoglobin precipitated at neutrality and dissolved in min. excess of alkali is entirely reprecipitated on neutralising with acid. A solution of methæmoglobin made alkaline after having been acid shows the spectrum of alkaline methæmoglobin irrespective of whether the protein is sol. or insol. at the isoelectric point. Determination of the alkaline methæmoglobin in such solutions yields curves which coincide with those obtained after "reversion" (A., 1925, i, 1475). Solutions are obtained at acid p_H which show spectra identical

with that of carboxyhæmoglobin but ppt. entirely on neutralisation. Determination of the amount of native protein measured by the intensity of this spectrum yields curves similar to those obtained when the natural protein is determined as alkaline methæmoglobin or when it is subjected to " reversion." It has been confirmed that the temp. at which denaturation takes place has little effect on the yield of native material after treatment with alkali and that the extent of denaturation is unaffected by length of treatment with acid after the first few min. — S. S. ZILVA.

Effect of acid-denaturation on the combining power of fibrinogen. M. FAY and B. M. HENDRIX (J. Biol. Chem., 1931, **93**, 667—675).—Fibrinogen from ox-blood is denatured by HCl at p_π 2·5—3·5 for 12—15 hr. at 12—14°, the isoelectric point being changed from p_H 4·7 to 5·2 and the acid- and base-combining powers diminished. — F. O. HOWITT.

Blood-protein precipitants. E. K. DOAK, G. BOONE, and F. PAQUIN, jun. (J. Lab. Clin. Med., 1931, **16**, 594—596).—There appears to be no const. variation in the concentrations of the non-protein-N of filtrates of (normal, nephritic, or eclamptic) blood precipitated by Na_2WO_4 and H_2SO_4, molybdic acid, tungstomolybdic acid reagents, or Folin's reagents for unlaked blood. Ergothioneine was not found. Tyramine was found in traces in blood of eclampsia. — CHEMICAL ABSTRACTS.

Serum-proteins. A. SCHMITZ (Biochem. Z., 1931, **241**, 271—272).—The results of Lustig on the globulin and albumin fractions of serum (A., 1930, 1607; this vol., 505, 640) are critically discussed. — P. W. CLUTTERBUCK.

Finger-blood method for micro-Kjeldahl [determination of] non-protein-nitrogen. T. L. CANNIFF (Proc. Soc. Exp. Biol. Med., 1930, **28**, 348).—Blood (0·1 c.c.) is treated with Folin's H_2WO_4 reagent (10 c.c.) and centrifuged after 2—3 min.; the determination is performed on 5 c.c. and the NH_3 in the distillate determined colorimetrically. Finger-blood gives higher results than venous blood. — CHEMICAL ABSTRACTS.

Determination of xanthine and hypoxanthine in blood. W. H. COLE, W. H. ELLETT, and N. A. WOMACK (J. Lab. Clin. Med., 1931, **16**, 918—923).—Oxalated blood is incubated for 24 hr. with xanthine-oxidase (from milk), and the uric acid determined before and after treatment. The normal ratio of xanthine base to uric acid is 2 : 1. — CHEMICAL ABSTRACTS.

Ergothioneine content of the blood in health and disease. H. B. SALT (Biochem. J., 1931, **25**, 1712—1719).—The contents of uric acid and of ergothioneine are given. A differential method for the determination of the latter compound was employed. — S. S. ZILVA.

Histamine and histamine-like substances in blood. O. E. GUTTENTAG (Arch. exp. Path. Pharm., 1931, **162**, 727—738).—Blood or its EtOH extracts cause contraction of the guinea-pig's isolated small intestine and uterus, which is not abolished by atropine or by the action of NaOH : they do not lower the blood-pressure of the atropinised cat or contract the isolated rat's uterus. Histamine is therefore considered absent from blood. — F. O. HOWITT.

Diazotisable constituent of blood. A. FRIEDRICH and A. LEIMDÖRFER (Biochem. Z., 1931, **240**, 430—440; A., 1924, i, 1126).—From blood corpuscles two diazotisable constituents can be obtained. One, which reacts at once with the diazotising reagent and yields a dinitrophenylhydrazone, is probably the parent substance of the chromogenic constituent. The other constituent accumulates slowly as a result of decomp. (possibly oxidation) of some material originally present. Long boiling with conc. alkali or mild oxidation with $KMnO_4$ seems to accelerate its formation. — W. McCARTNEY.

Determination of blood-fat, with observations on several species in post-absorptive conditions. H. E. HIMWICH, H. FRIEDMAN, and M. A. SPIERS (Biochem. J., 1931, **25**, 1839—1844; cf. A., 1925, i, 1485).—The experimental error of the method is ± 11 mg. per 100 c.c. The average val. for dogs in the post-absorptive state is 673 mg. per 100 c.c. The level of blood-fat varies by $\pm 3\cdot6\%$ in the course of an observation period of 8 hr. The vals. for blood-fat in post-absorptive conditions vary widely in the dog; the average vals. differ in various species. The method does not determine the fatty acids which exist in the blood as soaps, but only those as esters. — S. S. ZILVA.

Individual variation of fasting blood-sugar. G. W. HOLT and E. M. GREISHEIMER (Proc. Soc. Exp. Biol. Med., 1931, **28**, 764—765).—In normal man the day-to-day individual variation is as great as the group variation. — CHEMICAL ABSTRACTS.

Blood-sugar curves with acid and alkaline diets after administration of sugar by mouth. E. T. MINKER-BOGDANOVA (Russ. J. Physiol., 1931, **14**, 1—9).—Small alterations in the acidity and alkalinity of the diet of children do not appreciably affect the height of the blood-sugar curve after the administration of dextrose by mouth provided that the diet contains sufficient carbohydrate, but if the diet contains little carbohydrate and much meat abnormally high curves are obtained. — W. O. KERMACK.

Interferometric determination of alcohol in [normal] blood. J. C. BOCK (J. Biol. Chem., 1931, **93**, 645—655).—Blood is deproteinised with H_2MoO_4, distilled, and EtOH determined in the distillate by means of the interferometer. — F. O. HOWITT.

Occurrence and determination of oxalic acid in blood. W. MERZ and S. MAUGERI (Z. physiol. Chem., 1931, **201**, 31—37).—Determination of $H_2C_2O_4$ in the Et_2O extract is untrustworthy, as the extraction is incomplete. Trustworthy results are obtained by precipitation with lime-water after deproteinisation of the blood with $CCl_3\cdot CO_2H$. $MgSO_4$ is added to protect the ppt. with hydroxide or phosphate during washing. The titration follows Leulier's method (A., 1929, 614). $H_2C_2O_4$ is regularly present in normal ox-blood. — J. H. BIRKINSHAW.

Existence in blood of iron not combined with hæmoglobin. G. DOMINICI (Rend. Accad. Med. Torino, 1929, 6 pp.; Chem. Zentr., 1931, i, 3480).—

Normally the blood-non-hæmoglobin-Fe amounts to 0·92—3·12 mg. per 100 c.c. The val. increases in disease, particularly in that of the blood or liver.
A. A. Eldridge.

Relation of the concentration of calcium to that of protein and inorganic phosphate in the serum. I. Greenwald (J. Biol. Chem., 1931, 93, 551—561).—The equation, serum-Ca=[5+0·875(protein, mg. per 100 c.c.)] mg. per 100 c.c., has been applied to normal and pathological sera and only in a few instances yields vals. more accurate than those from other equations previously suggested (A., 1927, 416; 1929, 1478). An attempt to derive an equation agreeing with all types of sera was unsuccessful.
F. O. Howitt.

Hæmoglobin and total phosphorus in the blood of cows and bulls. C. M. McCay (J. Dairy Sci., 1931, 14, 373—378).—The hæmoglobin, Fe, and P contents of the blood of lactating cows is not affected by the level of protein feeding or by changes from winter conditions to pasture or sunlight. The blood of cows contains 10·9±0·86 g. and of bulls 12·8±0·8 g. of hæmoglobin per 100 c.c.
A. G. Pollard.

Blood of normal sheep. A. Trautmann, P. Luy, and J. Schmitt (Biochem. Z., 1931, 241, 260—270).—Many determinations on the blood of more than 100 sheep and a few goats are tabulated and differences due to age, sex, etc. noted. The following figures give the range of vals. for the different animals and the figures in parentheses the mean determination: Ca, 8—12 mg. per 100 c.c. (10·44); P, 5—10 mg. per 100 c.c. (7·43); sp. gr. at 18°, 1·0212—1·0293 (1·0250); p_H 7·4—7·58 (7·48); serum viscosity, 1·53—2·18 (1·70); blood viscosity, 4·0—5·4 (4·72); lowering of f. p. of venous blood, −0·535° to −0·60° (−0·567°); venous blood-sugar, 40—100 mg. per 100 c.c. (63·9); residual N, 13·2—40·6 mg. per 100 c.c. (28·1); plasma alkali reserve, 38·8—57·5 vols. CO_2 as $NaHCO_3$ per 100 c.c. of plasma (47·86).
P. W. Clutterbuck.

Refinement of Hastings and Sendroy's determination of p_H of blood. J. W. Schoonover and G. E. Woodward (J. Lab. Clin. Med., 1931, 16, 621—624).—The tubes are graded according to internal diameter, and the p_H of the saline indicator is adjusted with 0·01N-NaOH containing suitable amounts of phenol-red and NaCl. Chemical Abstracts.

Tonicity of blood of aquatic animals. W. J. Dakin and E. Edmonds (Austral. J. Exp. Biol., 1931, 8, 169—187).—The mangrove crab, *Helœcius cordiformis*, has the power of regulating its blood salinity. The body-wall of *Onchidium* acts like a semipermeable membrane.
A. Lawson.

Phosphatases of blood. J. Roche (Bull. Soc. Chim. biol., 1931, 13, 840—855).—The optimum p_H of the phosphatases of the erythrocytes, leucocytes, and serum of the horse have been determined; whereas the last two are identical, that of the first varies with the nature of the substrate. It is suggested that animal phosphatases are divisible into at least 2 groups, the first those from the erythrocytes, and the second those from serum, leucocytes, kidney,

and intestine. Bone-phosphatase is possibly a third group.
C. C. N. Vass.

Effect of anticoagulants on serum-enzymes and on complement. K. Yanagisawa (J. Biochem. Japan, 1931, 13, 11—42).—Heparin has no effect on guinea-pig serum-butyrase, -lecithinase, -cephalinase, -glycerophosphatase, -tryptase, -peptase, -nuclease, -amylase, or the glycolytic enzyme systems. Its effect on hæmolysis is discussed.
Chemical Abstracts.

Muscle coagulins. A. Fischer (Biochem. Z., 1931, 240, 357—363).—Aq. extracts of the breast-muscle tissue of the hen contain material which reduces the time of coagulation of hen's blood from several hr. (or days) to about 3 min., and although the extracts are sensitive to O_2 and very rapidly lose their activity, the dry material obtained by evaporation retains its power for more than 2 years. H_2O_2 and $KMnO_4$ destroy the activity of the aq. extracts, not at once, but suddenly after 24 hr. or longer. The aq. extracts are unstable and deposit flocculent matter, even at 0°, and the rate of deposition increases with rise of temp., becoming almost instantaneous at 56°. The active material passes to the deposit when solutions are boiled or heated for a long time at 56°. Heparin retards the deposition and at the same time reduces the activity, but has no effect on the activity of the deposited materials.
W. McCartney.

Mechanism of the inhibition of blood coagulation. A. Fischer (Biochem. Z., 1931, 240, 364—380; cf. preceding abstract).—Small amounts of substances (such as heparin, germanin, sulphosalicylic acid, and many others) which inhibit the coagulation of blood not only inhibit also precipitation of protein (globulin), but even cause peptisation of protein already precipitated. Heparin inhibits the precipitation at dilutions of $1:3\times10^6$ or less. Still smaller amounts of the substances, on the other hand, assist both precipitation of protein and coagulation of blood. The substances also cause a shift to the acid side in the isoelectric point of the protein and of the optimum point for coagulation of the blood. The mols. of all the substances which inhibit blood coagulation consist of a large org. complex to which strongly electro-negative groups (e.g., SO_3H) are attached. It is concluded that as regards their effects on precipitation of protein and on coagulation of blood the mechanism of action of the substances is the same and that a relation exists between blood coagulation and the synthesis and degradation of protein by the cells.
W. McCartney.

Influence of lactic acid on hæmolysis. J. Sládek, I. A. Parfentiev, and B. Sokolov (J. Pharm. Exp. Ther., 1931, 43, 245—250).—The hæmolysis of red blood-cells of rabbits in hypotonic NaCl solution is reduced by small concentrations of Na lactate. Thus with 0·4% aq. NaCl the degree of hæmolysis was reduced when the concentration of Na lactate was of the order of 0·1, whilst with lower concentrations of NaCl larger quantities of Na lactate were required. At p_H 7·0 Na lactate alone inhibits hæmolysis when present in concentrations greater than about 0·5%, whilst at p_H 5·0 about 1% Na lactate is required, and hæmolysis when it occurs is accompanied

by the decomp. of the hæmoglobin. The effect of Na lactate cannot be accounted for solely by the changes of osmotic pressure involved.   W. O. KERMACK.

Spectrographic analysis of human tissues. J. H. SHELDON and H. RAMAGE (Biochem. J., 1931, 25, 1608—1627).—195 specimens of different human tissues, both healthy and diseased, were examined. Cu, which is universal, occurs in greater concentration in fœtal tissues than in adult, and reaches its max. amount in the fœtal liver, where the percentage may be as much as ten times in excess of that present in the maternal liver. Mn occurs occasionally in many tissues, but is chiefly conc. in the liver, pancreas, suprarenal, and kidney. Fœtal bile contains a higher proportion than adult. In blood it is confined to the serum. Rb is almost as widely distributed as Cu and occurs in greatest concentration in the heart and in striated muscle. Ag, which is distributed to a smaller extent, is a normal constituent of the thyroid and the tonsil. Pb, Sr, and Li occur only occasionally.
S. S. ZILVA.

Absorption spectrum of medullated and non-medullated nerves. B. R. MONAGHAN and F. O. SCHMITT (Proc. Soc. Exp. Biol. Med., 1931, 28, 705—708).—Non-medullated nerves (claw of *Homarus* and *Limulus*) exhibited a spectrum characteristic of hæmochromogen compounds. The muscles of *Homarus*, *Limulus*, and green frog exhibit the spectrum typical of cytochrome. The sciatic nerves of frogs perfused with Ringer solution before dissection did not show the spectra of cytochrome or hæmochromogen, but showed bands due to carotenoid pigment (estimated, 0·5 mg. of carotene per g. of dry nerve), which may play an important part in the oxidative processes.   CHEMICAL ABSTRACTS.

Chemical nature of the tigroid. A. SZENT-GYÖRGYI (Nature, 1931, 128, 761).—Experiments suggest that tigroid is a reserve polysaccharide of the nervous tissues, similar to but not identical with glycogen.   L. S. THEOBALD.

Collagen substances in human arteries at various ages. A. M. TROITZKA-ANDREEVA (Arkh. biol. Nauk, 1930, 30, 519—526).—The collagen gradually increases in amount with increasing age. No relation of the process to senile atherosclerosis could be demonstrated.   CHEMICAL ABSTRACTS.

Composition of human fat. A. J. MCAMIS and W. E. ANDERSON (Proc. Soc. Exp. Biol. Med., 1931, 28, 749).—Fat from the abdominal wall of an obese female child (3 yr.) contained unsaponifiable matter 0·4%, saturated fatty acids 31·0%, and unsaturated fatty acids 60·0% (I val. 102).
CHEMICAL ABSTRACTS.

Differentiation of various types of fats by means of dyes. L. D. HERBERT (J. Lab. Clin. Med., 1931, 16, 926—929).—A routine method for the detection of fatty acids, neutral and acid fats, neutral Ca soaps, meat fibres, and cholesterol in fæces is described.   CHEMICAL ABSTRACTS.

Hydrocarbon in ishinagi-liver oil. M. TSUJI-MOTO (Bull. Chem. Soc. Japan, 1931, 6, 237—239).—A crude *hydrocarbon*, $M=612$ (camphor), 644 (C_8H_6) [*polybromide*, blackens and sinters at 170° after darkening from 130°; *polyhydrochloride*, m. p. 128—129° (decomp.) after sintering above 120°], is isolated in small amount from the unsaponifiable matter of the liver oil of *Stereolepis ishinagi*, Hilgendorf.
H. BURTON.

Lipins in the embryonic chicken liver. H. KIRKMAN (J. Amer. Inst. Homœopathy, 1931, 24, 508—510).—Osmiophilic granules, presumably fat or lipin, appear in the hepatic cells at the 7th or 8th day of incubation.   CHEMICAL ABSTRACTS.

Lipins of bone-marrow. L. T. CHENG (Z. physiol. Chem., 1931, 201, 209—218).—The lipins of various samples of bone-marrow were examined. The fatty acids consist principally of palmitic, stearic, and oleic acids with a small amount of arachidic acid. A fatty acid of high mol. wt. may be present. The lipins in the gelatinous marrow are more unsaturated than those in the fatty marrow. The lipins of fatty ox-marrow are more unsaturated than those of body-fat.   J. H. BIRKINSHAW.

Factors affecting size and iodine content of the thyroid in fowls. E. M. CRUICKSHANK (Proc. IV World's Poultry Cong., 1930, 237—241).—The max. I content is reached in 25—30 weeks; the seasonal variation in thyroid wt. is from 0·085 g. (March—July) to 0·13 g. (Jan.—March).   CHEMICAL ABSTRACTS.

Distribution of protein in squab and pigeon flesh. R. C. ELMER, F. C. HILBERG, and P. E. HOWE (Proc. IV World's Poultry Cong., 1930, 301—307).—The protein content is similar to that of chicken and lower than that of beef muscle. Squab flesh contains the higher proportion of sol. protein-N and H_2O.
CHEMICAL ABSTRACTS.

Hydroid pigments. *Sertulariidæ*. N. M. PAYNE (J. Marine Biol. Assoc., 1931, 17, 739—749).—The pigments of various species of *Sertulariidæ* are H_2O-sol. and belong to the flavone series. Their solubilities, coloured metal-salt additive compounds, and behaviour as indicators are described.
A. COHEN.

[Origin of] arcaine. L. ZERVAS and M. BERGMANN (Z. physiol. Chem., 1931, 201, 208; cf. this vol., 1178).—Since arginine can form ornithine and di-guanidovaleric acid (A., 1928, 874), the latter may be the precursor of arcaine.   J. H. BIRKINSHAW.

Occurrence of choline in the placenta. E. KOTTLORS (Zentr. Gynäkol., 1929, 2987—2990; Chem. Zentr., 1931, i, 2890).—During pregnancy the choline content of the placenta is approx. const. (60—90 mg. per kg.).   A. A. ELDRIDGE.

Composition and formation of bone skeletal substance. T. GASSMANN (Z. physiol. Chem., 1931, 201, 284).—A reply to Klement (this vol., 861). The disappearance of Ca, PO_4''', and CO_3'' in the ratio 10 : 6 : 1 from rhachitic bones can be accounted for only on the assumption of a complex of the constitution postulated by the author (A., 1913, ii, 320).
J. H. BIRKINSHAW.

Distribution of non-electrolytes between the blood and the cerebrospinal fluid. J. R. COCK-RILL (Arch. Neurol. Psych., 1931, 25, 1297—1305).—Dextrose, creatinine, uric acid, and urea are unequally distributed between the H_2O of the cerebrospinal

fluid and that of the plasma in man. The amounts in the neural fluid are 50—80% of those in the plasma. Urea is also present in dissimilar concentration in the cerebrospinal fluid and plasma of normal cats and cats with experimental uræmia. Plasma dialysed *in vitro* against cerebrospinal fluid from the same subject does not show this unequal distribution.

CHEMICAL ABSTRACTS.

Inorganic constituents of cerebrospinal fluid. I. Calcium and magnesium. R. A. McCANCE and E. WATCHORN (Quart. J. Med. 1931, 24, 371—379).—The Mg concentration is very const. (3.33 ± 0.19 mg. per 100 c.c.); it is not altered by presence of excess of protein, by syphilis, or by wide variations in the serum val. Not more than 80% of the serum-Mg is unfilterable. CHEMICAL ABSTRACTS.

p_H **of the cerebrospinal fluid.** R. CERNATESCO and A. MAYER (Ann. Sci. Univ. Jassy, 1931, 16, 551—554).—The mean p_H (quinhydrone electrode) is 7·08, and does not vary with time or on dilution of the fluid. The H electrode does not yield satisfactory results, possibly because of loss of CO_2.

H. F. GILLBE.

Determination of bile acids in bile. S. NAKAGAWA and H. FUJIKAWA (J. Biochem., Japan, 1930, 12, 399—410).—If the bile is made strongly alkaline with aq. NH_3 and a little Na_2CO_3 to facilitate filtration it can be treated with animal charcoal in the extraction of the bile acids with EtOH. The red colour produced by H_3PO_4 and furfuraldehyde is practically sp. for bile acids and is probably a reaction of cholic acid. Good results are obtained with human or dog's bile, but for rabbit's bile the results are low.

CHEMICAL ABSTRACTS.

Effect of bile acids on the salt excretion in the liver bile. Y. KAWADA (J. Biochem., Japan, 1931, 13, 133—144).—Na cholate when fed to dogs (0·05 g. per kg.) increases the ash and dry residue of fistula liver bile; the excretion of H_3PO_4 and Ca in the bile is increased. CHEMICAL ABSTRACTS.

Fluorescence spectra of pigments of the urobilin group. C. DHÉRÉ and J. ROCHE (Compt. rend., 1931, 193, 673—676).—Examined in the solid state, by means of a C arc or in ultra-violet light (λ 365 mμ), mesobilirubin, mesobilirubinogen, and urobilin show a red fluorescence, whilst EtOH solutions of mesobiliviolin, mesobilirubinogen, and urobilin with the addition of $Zn(OAc)_2$ show yellowish-green fluorescence for the first two cases, and green in the case of urobilin. The spectra of EtOH solutions containing $Zn(OAc)_2$ and a trace of AcOH show in the case of mesobiliviolin three absorption bands having axes at 629·2, 572·5, 505·1 mμ, and four fluorescence bands at I 640·4, II 592·3, III 553·0, IV 515·5 mμ, the order of decreasing intensity being I, IV, III, II. Mesobilirubinogen under the same conditions has three absorption bands at 629, 576, 507·5 mμ, and four fluorescence bands I 633·1, II 600·7, III 550·6, IV 520·9 mμ, I and II being very weak. Urobilin under the above conditions shows an absorption spectrum similar to the first two, the bands at 631 and 582 mμ being less marked. The fluorescence bands occur at I 502, and II 633, changing to 637 mμ. The EtOH solutions of the $HgCl_2$ complexes formed

by mesobiliviolin give absorption bands at 611, 563, 507 mμ, and fluorescence bands at 640 and 554 mμ, whilst the mesobilirubinogen Hg complex has absorption bands at 620, 570, 515 mμ, and fluorescence bands at 635·5, and 554·5 mμ, those in the orange range being strong, and in the green range weak. Under the same conditions urobilin and hydrobilirubin give no apparent fluorescence. A. LAWSON.

Conductivity of cod-liver oil. J. W. BUTLER (Proc. Iowa Acad. Sci., 1930, 37, 316—317).—The conductivity increases with rise of temp. Sharp breaks in the rectilinear temp.–log resistance curves occurred at different temp. in different tests. The resistance became unstable at about 85°. Exposure to air caused marked changes. No relation between the electrical conductivity and vitamin content was observed. Cod-liver oil is not photo-electric under the action of ultra-violet light.

CHEMICAL ABSTRACTS.

Gastric analysis in childhood. H. DIETRICH and D. C. SHELBY (Amer. J. Dis. Children, 1931, 41, 1086—1099).—The fractional method is employed; vals. for free HCl and total acidity show wide variations in normal children. CHEMICAL ABSTRACTS.

Composition of vixen milk. E. G. YOUNG and G. A. GRANT (J. Biol. Chem., 1931, 93, 805—810).—The composition of the milk and colostrum is given. F. O. HOWITT.

Citric acid in human milk. E. JERLOV (Svenska Läkartid., 1929, 17 pp.; Chem. Zentr., 1931, i, 2899).—Citric acid is not detectable in human milk before the third day after parturition; thereafter it increases, the quantity varying from 0·35 to 1·25 g. per litre. A. A. ELDRIDGE.

Effect on milk yield of feeding irradiated yeast. H. M. KROON (Milch. Zentr., 1931, 60, 325—328).—By feeding with irradiated yeast cows which had calved 3 weeks previously the weekly milk yield was increased by 25—30%, although there was no effect on the fat content of the milk. P. G. MARSHALL.

Influence of sunlight on milk. H. R. WHITEHEAD (Biochem. J., 1931, 25, 1647—1652); cf. A., 1930, 947).—The oxidation of fat in whole milk under the influence of sunlight causes the development of a poorly poised reducing potential of small capacity which can be detected either by its effect on methylene-blue or by electrometric measurement. Some samples of separated milk also show a fall in potential with a subsequent drift to more positive potentials. Ultra-violet radiation or radiation from electric lamps does not produce these effects. S. S. ZILVA.

Modification of Rothera's test for acetone substances in the urine. S. G. ROSS (J. Lab. Clin. Med., 1931, 16, 908).—The urine is treated with solid Na nitroprusside and $(NH_4)_2SO_4$. CHEMICAL ABSTRACTS.

Fermentable sugar in normal urine. V. J. HARDING and D. L. SELBY (Biochem. J., 1931, 25, 1815—1838).—Fermentable sugar is absent from normal fasting urine. After dextrose ingestion in the morning under fasting conditions no increased amount of fermentable sugar can be detected in the urine.

There are small amounts of fermentable sugar in the post-prandial afternoon urine of 50% of cases. Fermentable urinary sugar occurs after large amounts of fruit, orange juice, honey, or invert-sugar taken fasting, although in the first case this did not occur after dextrose in the morning or after ordinary mixed meals. 50 or 25 g. of pure lævulose given as a lævulose tolerance test in the morning or in the afternoon at 4 p.m. give rise to fermentable urinary sugar. 50 g. of dextrose at 4 p.m. frequently give rise to glycosuria in individuals showing none under the fasting conditions of the morning test. This is least likely to occur if the noon meal is high in carbohydrate, and most likely if the meal is high in protein or in fat. The blood-sugar curves at 4 p.m. taken under ordinary conditions of diet all possess a higher peak than the corresponding fasting morning tolerance curves. The peak often rises above the usual renal threshold of sugar. The nature of the noon meal affects the blood-sugar curve after 50 g. of dextrose at 4 p.m. A high-carbohydrate meal gives rise to the lowest curve, a high-fat meal to a high-peak curve, sometimes remaining high at the end of 2 hr. There was ketosis in 6 out of 8 experiments after a high-fat noon meal. A high-protein noon meal gives a high-peak blood-sugar curve. All tolerance curves at 4 p.m. are higher than the morning tolerance curve in the same individual. There is no afternoon glycosuria in the urine after oral administration of lævulose. The non-occurrence of glycosuria after the usual morning dextrose tolerance test cannot be taken as a criterion of its continued non-occurrence throughout the day. S. S. ZILVA.

Determination of urinary sugar. J. E. COOK and A. STEINER (J. Lab. Clin. Med., 1931, 16, 629—631).—The amount of $CuSO_4$ required to produce turbidity in urine containing 5% NaOH is measured. CHEMICAL ABSTRACTS.

Detection of lactosuria by the Castellani–Taylor mycological method. F. W. WILLWAY (J. Trop. Med., 1931, 34, 133—134).—Urine which reduces Fehling's solution and is fermented by B. coli but not by B. paratyphosus contains lactose. The method is very sensitive. CHEMICAL ABSTRACTS.

Urinary composition and acid–base equilibrium. III. S. M. NEUSCHLOSZ (Biochem. Z., 1931, 240, 286—294; this vol., 644).—The processes formerly used were inadequate, since the buffering effect of the org. acids of the urine was not taken into account. Results obtained by an appropriately modified procedure agree better with theory than did former results, but do not affect the dependence of the vals. on the [H˙] of the urine or the relations between the vals. W. MCCARTNEY.

Urinary acidifiers and alkalinisers. V. E. HENDERSON and J. M. SCOTT (Canad. Med. Assoc. J., 1931, 24, 833—834).—Acidity is produced by administration of NaH_2PO_4, NH_4OBz, or NH_4Cl, and alkalinity by that of acetates or citrates. CHEMICAL ABSTRACTS.

Micro-determination of fixed bases, calcium, and sulphates in urine. W. S. HOFFMAN (J. Biol. Chem., 1931, 93, 787—796).—Protein, inorg. and org. phosphates, fat, and some of the urinary pigments are removed by boiling with $FeCl_3$ in presence of NH_4OAc and filtering. The filtrate is ashed and SO_4 determined by the method of Stadie and Ross (A., 1926, 100) or directly on the filtrate by the method of Fiske (A., 1921, ii, 556). Ca is determined in the filtrate by precipitation as CaC_2O_4 and titration by $KMnO_4$. Comparative data are given. F. O. HOWITT.

Determination of total fixed base, sodium, and potassium in urine. A. FØLLING (Skand. Arch. Physiol., 1931, 61, 27—34; Chem. Zentr., 1931, i, 3030).—The total base (in 2 c.c.) and the Na+K (in 10 c.c.) are determined by Stadie's benzidine method; the Na (in 5 c.c.) is precipitated as $NaZn(UO_2)_3(OAc)_9,9H_2O$, and determined titrimetrically. A. A. ELDRIDGE.

Determination of magnesium and of calcium in urine by the step photometer. C. URBACH (Biochem. Z., 1931, 241, 222—225, 226—227).—The methods are described and claimed to be superior to the colorimetric methods. The errors are ±6·2% for Mg and ±3% for Ca determinations. P. W. CLUTTERBUCK.

Determination of ammonia in urine by extraction. G. HAMMARSTEN (Skand. Arch. Physiol., 1931, 61, 49—63; Chem. Zentr., 1931, i, 3030).—In order to avoid high vals. resulting from decomp. of nitrogenous substances, especially urea, the NH_3 is extracted with Et_2O at room temp., and again extracted with $0·1N$-H_2SO_4, the excess of which is then titrated. A. A. ELDRIDGE.

Colorimetric determination of uric acid in urine. H. B. SALT (Biochem. J., 1931, 25, 1720—1723).—A modification of Folin's method which obviates turbidity in the final colours is described. S. S. ZILVA.

Direct determination of urea in urine. S. W. COLE (Biochem. J., 1931, 25, 1653—1655).—A modification of Marshall's method (A., 1913, ii, 640) in which a stronger enzyme prep. is used and the medium is maintained under optimal conditions of reaction. It is possible to complete the determination in 20 min., and the results are accurate to within 2%. S. S. ZILVA.

Glucose tolerance in pernicious anæmia. T. A. C. RENNIE (J. Lab. Clin. Med., 1931, 16, 557—560).—Low vals. are often observed. CHEMICAL ABSTRACTS.

Certain lipoidal fractions of the adenocarcinoma of the rat. A. BOLAFFI (Atti R. Accad. Lincei, 1931, [vi], 13, 298—300).—The aq. $COMe_2$ (d 0·85) extract of a tumour (rat adenocarcinoma, Ehrlich strain) has been analysed, together with the whole bodies of both normal and tumour rats. The total matter extracted by the solvent is reduced in the cancerous rat and still more in the cancerous tissue from that given by the normal rat. The soaps present in the appreciably lower proportion of neutral fats in the affected animals are in relatively higher amount, the K soaps especially showing a marked increase. The cancerous rats contain 2—3 times as much as the healthy ones of a base, which is united to the lipins and gives a cryst. salt with $HgCl_2$ and is precipitated by phosphotungstic acid. A phos-

phatide (1% P, I val. 58·7) is more abundant in the healthy than in the diseased animal or the tumour itself. A sulphophospholipin (S 1·5, P 1·06%), containing a base (? choline or cholamine), a highly unsaturated acid (probably linolenic) radical, and possibly lignoceric acid, occurs in higher concentration in the tumour than in the whole affected organism; the normal rat contains only traces. T. H. POPE.

Lipin content of malignant tumours. E. BIERICH, A. DETZEL, and A. LANG (Z. physiol. Chem., 1931, **201**, 157—166).—Carcinomatous tissue has a very high content of cholesteryl esters (C) and a slightly increased phospholipin content (P) as compared with normal tissue. In benign tumours both (C) and (P) are lower; in both types of tumour the quotient (P/C) is small. J. H. BIRKINSHAW.

Carbohydrate metabolism in malignant tumours. I. S. YUN and Y. C. LEE (Trans. Japan. Path. Soc., 1930, **20**, 734—737).—Hyperglycæmia usually occurs in sarcoma rabbits after inoculation of tumour tissue. The sensitivity to adrenaline, insulin, and pilocarpine is described. The variations in blood-sugar may be caused by glycolysis of tumour tissue *in vivo*. CHEMICAL ABSTRACTS.

Capacity of extracts of minced normal and malignant tissue to take up oxygen. K. VIETO-RISZ and A. SZENT-GYÖRGYI (Biochem. Z., 1931, **240**, 480—487).—The ability of suspensions of minced normal (liver, heart, muscle, testis, kidney, brain) and diseased (Ehrlich mouse carcinoma, Jensen rat sarcoma, Rous chick sarcoma) tissue before and after successive centrifuging and filtration to take up O_2 and to oxidise succinic acid has been investigated. In all cases both respiratory and oxidising powers are reduced by centrifuging and (except in the cases of the otherwise untreated heart muscle and testicular tissues) further great reduction results from filtration, but if the suspensions are ground with sand the effect of centrifuging and filtering is usually considerably less pronounced. The filtrates from the rat sarcoma and the mouse carcinoma give negative results when injected into rats and mice, respectively. Probably the respiratory power of the filtrates varies in proportion to their turbidity and is a function of the "optically visible parts" of the protoplasm. W. McCARTNEY.

Tissue proteases. III, IV, V. Proteolytic enzymes of human malignant tumours. H. KLEINMANN and E. WERR (Biochem. Z., 1931, **241**, 108—139, 140—180, 181—217).—Existing knowledge of the proteolytic enzymes of normal and malignant tissues is reviewed and the proteolytic enzymes of human malignant tissue (carcinoma, sarcoma) are compared qualitatively and quantitatively with those of normal tissue. A detailed description of the nephelometric micro-method for investigation of tissue proteases is given. It is the only sure method of separation of the action of tryptase and ereptase and enables the degradation of proteins to be followed, not in terms of hydrolysis products, but in terms of the degradation of the substrate itself. Methods for the enzymic degradation of gelatin, caseinogen, edestin, and serum-albumin are developed. Acid and alkaline, aq. and glycerol enzyme extracts of the tissues were tried, but acid glycerol extracts proved most useful. The cathepsin, trypsin, and ereptase contents of the extracts were obtained. Extracts of tumour tissue were quantitatively compared with extracts of ox spleen and of human tissue (spleen, liver, kidney, brain, muscle, skin). Both normal and tumour tissue contain chiefly cathepsin with small amounts of trypsin. A kinetic study of the degradation of gelatin and caseinogen by cathepsin of normal and tumour tissue did not detect any difference between them. All the extracts of normal and tumour tissue showed two optima at p_H 3 and 5 against caseinogen. Strong extracts (of ox spleen and human parenchymatous organs) showed a third smaller optimum at p_H 8 (due to trypsin). Against gelatin, only the strong extracts showed any action, but after activation by H_2S all the extracts showed an optimum at p_H 4. All the extracts attacked edestin, the optimum being at p_H 4, but only the strong extracts attacked serum-albumin. All the extracts showed activation with H_2S and HCN when gelatin was used as substrate, but with the other proteins such activation did not occur. After purific-ation of the enzyme, the cathepsin of the eluate is still activated by H_2S, but not by HCN. Tumour tissue extracts are purified by the same methods as for normal tissue extracts and the purified enzyme gives the same p_H–activity curve as the unpurified and is activated only by H_2S with gelatin as substrate. All the evidence goes to show that neither qual. nor quant. differences exist between the extracts of normal and malignant tumour tissue as to their proteolytic powers. P. W. CLUTTERBUCK.

Autolysis in malignant and normal rabbit tissues. H. I. PRICE (Biochem. J., 1931, **25**, 1491—1497).—Robin's observation (Bull. Acad. Méd., 1919, **81**, 799) that the percentage ratio of protein-N to total N is lower in the "relatively healthy" region than in either the most cancerous region or the normal tissue does not manifest itself in freshly-excised tissue. After death H_2O disappears from the growth into the surrounding tissue. A malignant growth does not liberate proteolytic enzymes into the sur-rounding tissues. S. S. ZILVA.

Demonstration of a tumour-inhibiting sub-stance in filtrate of Rous chicken sarcoma and in normal chicken sera. M. J. SITTENFIELD, B. A. JOHNSON, and J. W. JOBLING (Proc. Soc. Exp. Biol. Med., 1931, **28**, 577—520).—The supernatant liquid after precipitation of the tumour-producing agent at p_H 4 contained a substance which reduced the percentage of tumours developed by inoculated chickens, but did not prevent the growth of living tumour cells. The substance was precipitated with the globulin fraction of the supernatant liquid. CHEMICAL ABSTRACTS.

Effect of arsenic and hydrocyanic acid on the respiration of malignant tumours. K. VIETORISZ (Biochem. Z., 1931, **240**, 488—489).—The respiration of malignant tumours is affected by H_3AsO_3 and by HCN in the same way as is that of normal tissues. W. McCARTNEY.

Hydrogen-ion concentration of blood in untreated cancer cases and its relation to prognosis. G. E. WOODWARD, J. W. SCHOONOVER, E. G. FRY, E. G. TORRANCE, and E. McDONALD (J. Lab. Clin. Med., 1931, **16**, 704—712).—The p_H of normal plasma or blood varies from 7·35 to 7·38. In skin and superficial cancer it is 7·38, and in untreated advanced cancer 7·44.   CHEMICAL ABSTRACTS.

Metabolism in celiac disease. O. MACRAE and N. MORRIS (Arch. Dis. Childhood, 1931, **6**, 75—93).—In celiac disease the ability of the intestines to absorb Ca, P, dextrose, and protein is impaired, probably owing to increased alkalinity of the contents, deficiency of bile salts, and lack of vitamin-D.
                    CHEMICAL ABSTRACTS.

Anæsthesia in diabetes. Carbon dioxide-combining power of blood-plasma before and after ethylene anæsthesia in diabetics protected with insulin. I. I. LEHMANN (Anesth. and Analg., 1931, 10, 142—144).—No post-operative CO_2 val. approaching that of acidosis was found.
                    CHEMICAL ABSTRACTS.

Lactic acid in the blood of children. J. S. LEOPOLD and A. BERNHARD (Amer. J. Dis. Children, 1931, **41**, 758—765).—The venous blood-lactic acid of normal children is 9—18 (average 14·8) mg. per 100 c.c. High vals. are associated with pneumonia, rheumatic fever, chorea, and high temp. No quant. relationship between the lactic acid concentration and the blood-sugar or -CO_2-combining power is observed.   CHEMICAL ABSTRACTS.

Cause of exophthalmic goitre. W. S. REVENO (Arch. Int. Med., 1931, **48**, 592—597).—It is suggested that in exophthalmic goitre toxic substances of intestinal origin damage the thyroid gland so that the metabolism of tyrosine becomes abnormal, an excess of thyroxine, adrenaline, and tyramine being produced.   W. O. KERMACK.

Iodine in exophthalmic goitre. J. LERMAN and J. H. MEANS (Amer. J. Med. Sci., 1931, **181**, 745—755).—I produces its characteristic effects independently of the type of compound (EtI, KI, or Lugol's solution) or the manner of administration.
                    CHEMICAL ABSTRACTS.

Hypocalcæmia following experimental hyperparathyroidism and its possible significance. A. BODANSKY and H. L. JAFFE (J. Biol. Chem., 1931, **93**, 543—549).—Discontinuance of parathyroid hormone treatment in young guinea-pigs is followed by a hypocalcæmia accompanied by changes in the P balance probably due to a rapid deposition of Ca in the bones depleted during the period of injection. A hypo-function of the glands induced by the hormone treatment may also play a part.   F. O. HOWITT.

Iron metabolism in liver disease with icterus. T. BRUGSCH (Med. Klinik, 1931, **27**, 536—539; Chem. Zentr., 1931, i, 3021—3022).—The high Fe content of the skin is due to deposition of Fe from the blood. The accumulation of Fe in the liver in icterus does not lead to increased elimination in the urine and bile. The intercutaneous $K_4Fe(CN)_6$ reaction may be produced by the oxidation of considerable quantities of bilirubin in the skin.   A. A. ELDRIDGE.

Detection of bilirubin in the skin in icterus. K. JEGOROV (Deut. med. Woch., 1931, **57**, 539—540; Chem. Zentr., 1931, i, 3030).—The use of $K_4Fe(CN)_6$ and of diazobenzenesulphonic acid for the detection of bile colouring-matters in the tissues is described.   A. A. ELDRIDGE.

Methylene-blue as reagent for bilirubin. M. ROCH (Med. Klinik, 1931, **27**, 589—590; Chem. Zentr., 1931, i, 3030).—Franke's methylene-blue reaction for the detection of bilirubin in urine is trustworthy. The colour change is attributed to a physical process.   A. A. ELDRIDGE.

Carbohydrate metabolism in Mongolian idiots as evidence of endocrine dysfunction. W. D. O'LEARY (Amer. J. Dis. Children, 1931, **41**, 544—551).—The high dextrose tolerance resembles that of a hypo-functioning endocrine system. Following glandular therapy the tolerance becomes normal or lowered and the curves resemble those of mild diabetes or hyper-function of the thyroid and pituitary glands.
                    CHEMICAL ABSTRACTS.

Blood-calcium in mental diseases. J. S. HEPBURN and A. H. NEIBAUM (J. Amer. Inst. Homeopathy, 1931, **24**, 559—560).—In dementia præcox blood-Ca is high (e.g., more than 11 mg. per 100 c.c.); in general paresis vals. were 10·5—11·0, and in epilepsy 10·0 or less.   CHEMICAL ABSTRACTS.

Blood of leucæmic subjects. Variation of lipins in leucæmia. S. MARINO (Arch. Farm. sperim., 1931, **53**, 17—52).—Diminished amounts of total fatty acids and cholesterol in the blood are found in chronic aleucæmic myelosis, whilst $COMe_2$-sol. fatty acids and phospholipins are unchanged. In chronic leucæmic myelosis and lymphadenosis the variations are irregular and bear no relation to the no. of leucocytes.   R. K. CALLOW.

Elimination of phenolsulphonephthalein by the kidney. Influence of pathologic changes in the liver. J. P. HANNER and G. H. WHIPPLE (Arch. Int. Med., 1931, **48**, 598—610).—When phenolsulphonephthalein is injected into a dog about 10% may be recovered from the bile in about 2 hr. and 75—78% appears in the urine. In the case of dogs with livers poisoned by $CHCl_3$ or P, secretion of the compound in the bile does not occur, and 90—97% is excreted in the urine. Only 3—5% of the phthalein taken by mouth appears in the urine. Reabsorption from the intestine therefore takes place only to a small extent, and abnormally high excretion of the phthalein in the urine by humans is indicative of hepatic disease.   W. O. KERMACK.

Water economy in disturbed liver function. I. Effect of the oral administration of water on the intermediate water metabolism and excretion in patients with liver disease and in dogs with damaged livers. S. ABE (Tôhoku J. Exp. Med., 1931, **17**, 174—218).—In normal man the serum-protein, -NaCl, and blood-hæmoglobin are minimal following the ingestion of H_2O within 30 min. Changes in blood concentration are recorded. In liver disease or injury there may be prolonged hydræmia.   CHEMICAL ABSTRACTS.

Absence of blood-uric acid in a case of liver damage. H. TAUBER (J. Amer. Inst. Homeopathy, 1931, 24, 515—516).—During the last 7 weeks of life the urine (d 1·013—1·025; 270—550 c.c. per day) contained total N 3·30—4·75 g., urea 4·50—8·10 g., tyrosine 120 mg., and marked amounts of bile, urobilin, and urobilinogen, but no albumin. The blood contained dextrose 55—62, non-protein-N 25—27, urea-N 5—8, and creatinine 1·3—1·6 mg., but <0·5 mg. of uric acid, per 100 c c.
CHEMICAL ABSTRACTS.

Metabolism in myotonia atrophica. S. MORGULIS and A. YOUNG (Arch. Int. Med., 1931, 48, 569—575).—A patient suffering from myotonia atrophica excreted in the urine an abnormally high quantity of creatine and an abnormally low quantity of creatinine, the total creatine and creatinine being approx. equal to the normal. A diet rich in arginine did not increase urinary creatine, but creatine taken by the mouth was rapidly and almost quantitatively excreted in the urine, about 16% appearing as creatinine. W. O. KERMACK.

Metabolism in nephrosis. D. M. COWIE, K. M. JARVIS, and M. COOPERSTOCK (Amer. J. Dis. Children, 1930, 40, 465—483).—A child with nephrosis associated with a high basal metabolic rate was free from œdema when a positive N balance of 1—3·76 g. was maintained. During this period the urinary albumin markedly decreased. The blood-protein rose to 5 g. per 100 c.c. before œdema permanently disappeared. CHEMICAL ABSTRACTS.

Lipin nephrosis. IV. Extraction of the serum-lipins by ether. A. MÂCHEBŒUF and R. WAHL. **V. The physico-chemical equilibrium and the rôle of plasma-lipins.** A. MÂCHEBŒUF and G. SANDOR (Bull. Soc. Chim. biol., 1931, 13, 736—744, 745—757).—IV. Extraction with Et_2O of normal and pathological sera does not remove the total lipin content even when the extraction is performed every 2 days for a period of 5 months. The greater is the protein content of the serum the less readily are the lipins extracted. Lipins are less readily extracted from normal than from pathological sera.

V. Comparison of the hydrophilic powers of normal and pathological sera at p_H 7·4, on the basis of dialysis, suggests that the combination of proteins and lipins, such as occurs in lipin nephrosis, liberates more free, non-diffusible, ionic valencies than an equal wt. of normal protein. The buffering action of the proteins admixed with lipins from lipin nephrosis is greater than that of an equal wt. of protein from normal sera, whilst the isoelectric points are identical.
C. C. N. VASS.

Absorption of calcium from the gall bladder. E. ANDREWS and L. HRDINA (Amer. J. Med. Sci., 1931, 181, 478—482).—In cystic duct obstruction in dogs the relatively high Ca content of the cystic bile is gradually, or in the presence of infection rapidly, lowered. CHEMICAL ABSTRACTS.

Cholesterol and œdema. J. K. CALVIN and A. H. GOLDBERG (Amer. J. Dis. Children, 1931, 41, 1066—1080).—The hypercholesterolæmia of renal disease is probably the result of a disturbance in fat metabolism accompanying the nephrotic syndrome.

The blood-cholesterol is high during, and sometimes after, œdema; the ascitic fluid- and bile-cholesterol is low. CHEMICAL ABSTRACTS.

Peroxidase reaction in pus. S. KONNO (Tôhoku J. Exp. Med., 1931, 17, 31—38).—The peroxidase reaction in pus from acute otitis media is usually similar to that of normal leucocytes. In chronic otitis media crystals are frequently found inside and outside the pus cells. CHEMICAL ABSTRACTS.

Pus and its calcium content. T. OYAMA (Tôhoku J. Exp. Med., 1930, 16, 438—485).—The Ca content of pus from abscesses does not exceed 12% unless bone is involved, when it may exceed 13—15%.
CHEMICAL ABSTRACTS.

Diastatic enzyme content of skin and blood. Its biochemical importance in skin diseases. I. Diastatic enzyme in the skin of healthy persons. II. Diastase in the skin in skin diseases and in diabetes. III. Diastase in blood. B. OTTENSTEIN (Biochem. Z., 1931, 240, 328—343, 344—349, 350—356).—I. The diastase content of the surface layer of the living undamaged human skin *in situ* can be measured by allowing the enzyme to pass during 5 min. into distilled H_2O at room temp. and determining the amount of enzyme in the solution so formed by a combination of the methods of Rona and Eweyk (A., 1924, i, 1264) and of Hagedorn and Jensen, using glycogen as substrate. The content varies according to the location of the skin and is dependent on the blood supply and on the amount of sweat secreted at the place concerned. The vals. also vary from person to person and, in the same person, from time to time. When carbohydrate is consumed or injected the amount of diastase in the dialysate increases and at the same time the reaction of the solution becomes more acid. Injection of insulin causes increase which changes to decrease in the diastase content. When the permeability of the skin is increased by the action of KOH the amount of diastase in the dialysate increases. Irradiation of the skin with ultra-violet light decreases the diastase content greatly. The significance of the results is discussed.

II. In ichthyosis the diastase content of the skin increases and in other skin diseases (eczema, dermatitis, psoriasis, etc.) abnormal contents are found after intravenous injection of dextrose or intramuscular injection of insulin. In diabetes the content is high, but falls together with the sugar content of the blood after administration of insulin.

III. In healthy persons the blood contains 130—170 mg. of diastase per 100 c.c., whilst in diabetics much lower vals. are found, especially when no insulin has been administered. The diastase content of persons suffering from certain skin diseases is also low. W. McCARTNEY.

Chloride metabolism in congenital pyloric stenosis. N. MORRIS and S. GRAHAM (Arch. Dis. Childhood, 1931, 6, 27—36).—Intravenous administration of NaCl tends to restore the reduced Cl content of the tissues; it may lead to excessive retention. Restoration of the blood-Cl to the normal level may be associated with a low urinary output with no reduction in the degree of alkalosis.

CHEMICAL ABSTRACTS.

Chemical analysis of blood in general and urologic surgery. V. C. MYERS (J. Lab. Clin. Med., 1931, **16**, 751—759).—A discussion of prognosis.
CHEMICAL ABSTRACTS.

Metabolism in typhoid. Trial of a causal treatment. J. KLEEBERG (J. Egypt. Med. Assoc., 1931, **14**, 543).

Pond life, with special reference to the possible causation of the swarming of phytoplankton. S. C. AKEHURST (J. Roy. Microscop. Soc., 1931, [iii], **51**, 237—265).—Phytoplankton can be classified as a starch group and an oil group, according to the nature of their food reserve. The author suggests that the excretory products of each class are toxic to that class, but form an accessory food for the other class.
C. W. GIBBY.

Action at a distance on the development of sea-urchin's eggs. J. MAGROU, M. MAGROU, and P. REISS (Compt. rend., 1931, **193**, 609—612).—The development of sea-urchin's eggs proceeds abnormally when the egg suspension is separated by a thin sheet of quartz from an aq. medium containing reduced phenosafranine, dextrose in presence of $KMnO_4$, or a bacterial suspension. Experiments with thin sheets of different materials indicate that the essential requirement for a positive result is that the two media should be separated by a good insulator. The action appears to depend on a difference in oxidation–reduction potential on the two sides of the insulating sheet.
W. O. KERMACK.

Is there a parallelism between function and metabolism in vegetative organs? F. MATAKAS (Arch. exp. Path. Pharm., 1931, **162**, 395—419).—Experimental and clinical observations indicate a negative answer.
W. O. KERMACK.

Sex differences from the point of view of biochemistry. I. T. TADOKORO (J. Fac. Sci. Hokkaido, 1930, **1**, 1—179).—A comprehensive statistical survey of sex differences in physiology, anatomy, and general metabolism. The muscle-tissue of females in various types of fish and animals shows a greater reducing power than that of males, whilst the latter has a greater peroxidase activity, which is diminished by castration. Female bone invariably contains more Ca and less P than male bone, whilst the collagen of the latter is richer in NH_2-acids, particularly arginine. Female muscle has a higher power of swelling in aq. KCl than male muscle owing to its different protein composition; acetylation reveals a larger OH-group content in female than in male muscle-protein, which may account for this phenomenon. The female proteins have a higher P content and greater solubility but a lower S content; their isoelectric point is more acidic and they exhibit a lower rotation in alkaline solution. The lesser pigmentation of the female in general is explained by the decreased peroxidase activity combined with the fact that the chromogen of melanin is fat-sol. and melanin formation is therefore delayed. Female fat contains a higher percentage of unsaturated fatty acids and unsaponifiable matter than male fat, but it has a lower sap. val. The absorption spectrum of male fat is shorter than that of female, but its n is always higher.
P. G. MARSHALL.

Thermodynamic theory of excitation of nerves. N. RASCHEVSKY (Physical Rev., 1930, [ii], **35**, 1435).
L. S. THEOBALD.

Liver metabolism. I. Continuous determination of the gas exchange of perfused isolated organs in a closed system. III. Gas exchange and equilibrium in the perfused isolated innervated or non-innervated liver. H. STAUB (Arch. exp. Path. Pharm., 1931, **162**, 420—427, 433—451).—I. The apparatus described uses an artificial lung, measures the rate of perfusion, and allows a continuous series of observations to be made.

III. The O_2 consumption of the dog's liver perfused with dil. ox blood has a mean val. of 26·5 c.c. per kg. per min. The mean CO_2 production is 20·2 c.c. per min. and the R.Q. is 0·44—1·04. Factors such as duration of previous fasting, the intactness or otherwise of the nerve supply, or the rate of blood-flow appear to have no significant effect. The liver loses glycogen, giving up dextrose to the blood and the liver- and blood-fat usually fall. The addition of dextrose to the perfusion fluid causes the R.Q. to rise with increase of CO_2 production and a negative carbohydrate balance is observed. The fat balance becomes positive. With 0·362% of dextrose in the blood, glycogen is deposited in the liver. The effect of the addition of glycine to the perfusion fluid has also been determined.
W. O. KERMACK.

Measurement of oxygen consumption, respiratory quotients, and reduction of methylene-blue by tissues and by yeast. P. AMBRUS, I. BANGA, and A. SZENT-GYÖRGYI (Biochem. Z., 1931, **240**, 473—477).—In the Barcroft apparatus the absorption of CO_2 is greatly facilitated by suspending filter-paper soaked in 20% aq. NaOH in the manometer tube. An apparatus for determining the absorbed CO_2 is described. The uptake of O_2 by minced muscle-tissue can be determined by measuring the corresponding dehydrogenation, and a procedure in which the reduction of methylene-blue provides this measure is described. Probably because of the time required for diffusion when methylene-blue and yeast suspensions react anaërobically for the first time, the period of reduction is always greater then than when the mixture is shaken with air until the dye is completely reoxidised and the experiment repeated. No decrease in the reduction period occurs when further repetitions are made.
W. McCARTNEY.

Importance of lactic acid for the respiration of minced heart-muscle. I. BANGA, L. SCHNEIDER, and A. SZENT-GYÖRGYI (Biochem. Z., 1931, **240**, 478—479).—The consumption of O_2 by minced pig-heart-muscle is increased by addition of lactic acid and inhibited by addition of $CH_2I \cdot CO_2H$, but the inhibition is only slight with concentrations of $CH_2I \cdot CO_2H$ which suppress production of lactic acid. It is concluded that the inhibiting effect of $CH_2I \cdot CO_2H$ on the respiration is not due to the accompanying inhibition of lactic acid production and that in minced heart-muscle lactic acid is not an indispensable intermediate oxidation product. The result also supports the view that oxidative and fermentative degradation proceed, for the most part, in different ways.
W. McCARTNEY.

Influence of the co-enzyme of lactic acid formation on the hydrolysis of carbohydrate phosphoric esters in muscle extracts. K. LOHMANN (Biochem. Z., 1931, 241, 50—66).—Frog's muscle extract after keeping at 20° for 3 hr. is no longer able to hydrolyse hexose-mono- and -di-phosphate and glycogen, but is reactivated by addition of adenylpyrophosphate. The dialysed extract can be reactivated by adding $Mg+$adenylpyrophosphate. Hydrolysis of diphosphate does not require added inorg. phosphate, but that of monophosphate is accelerated by addition of inorg. phosphate. Inactivated but not dialysed extracts can dephosphorylate hexosediphosphate to some extent without lactic acid formation. With dialysed extracts such dephosphorylation occurs only after addition of Mg salts.

P. W. CLUTTERBUCK.

Comparative investigation of the co-enzymes of lactic acid formation and of alcoholic fermentation. K. LOHMANN (Biochem. Z., 1931, 241, 67—86).—The co-enzyme of lactic acid formation can be precipitated in neutral solution from the deproteinised extract of fresh muscle as the sparingly sol. Ba salt. Its activity in both crude and purified preps. runs parallel with the pyrophosphate fraction. The co-enzyme of lactic acid formation of yeast can be similarly precipitated from AcOH solution as the Pb salt. Euler's cozymase can act as co-enzyme of lactic acid formation in inactivated frog's muscle extracts, but not in dialysed extracts. The cozymase is very much more active as co-enzyme of alcoholic fermentation than adenylpyrophosphate. Cozymase then requires the presence of hexosediphosphate, whereas the pyrophosphate does not. The org. components of the co-enzyme system of lactic acid formation and alcoholic fermentation are not identical, but both systems require the presence of Mg salts.

P. W. CLUTTERBUCK.

Relation between chemical exchange and increase of osmotic pressure in muscle. O. MEYERHOF and A. GROLLMAN (Biochem. Z., 1931, 241, 23—35).—The increase of osmotically active mols. as determined by changes of f. p. during fatigue of muscle is always 30% greater than is accounted for by known chemical changes. The f.-p. change is independent of muscle structure. At least $\frac{1}{4}$ of the excess is explained by side reactions, e.g., increase of NH_2-N and hydrolysis of glycogen. The osmotic activity of the hydrolysis products appearing in muscle is the same as in aq. solution and it must be concluded that other still unknown reactions occur.

P. W. CLUTTERBUCK.

Rigor in muscle and co-enzyme. H. K. BARRENSCHEEN, L. FREY, and O. RENTH (Biochem. Z., 1931, 240, 394—408).—In frog and guinea-pig muscle rigor mortis and also rigor caused by heat, caffeine, Et_2O, and $CHCl_3$ lead to complete or almost complete disappearance of the "pyrophosphate fraction" and hence also of the co-enzyme. This disappearance shows itself in the production and accumulation of methylglyoxal from added Mg hexosediphosphate and, in some cases at least, in inability of juice from the muscles in rigor to activate yeast free from co-enzyme. The rigor produced by heat, Et_2O, and caffeine also leads to accompany-

ing production of the difficultly hydrolysable phosphoric esters. Such production does not result from rigor mortis or from the rigor caused by $CHCl_3$ or by the prolonged action of caffeine. The results confirm views previously expressed (this vol., 647).

W. McCARTNEY.

Elimination of pentose in muscular work. G. EMBDEN and M. LEHNARTZ (Z. physiol. Chem., 1931, 201, 149—156).—The stimulation of frog's gastrocnemius to exhaustion produces a large increase in "alcohol-sol." pentose. When both muscles were equally stimulated one, examined after 2 hr. in O_2, contained more pentose than the other, examined immediately, even under conditions where re-formation of $H_4P_2O_7$ occurs during recuperation. A loaded muscle after immersion in liquid air contains more alcohol-sol. pentose than an unloaded muscle when so treated. This also applies when the contraction of the loaded muscle is augmented by electrical stimulation at the moment of immersion. The appearance of pentose is regarded as due to hydrolysis of pentosephosphoric acid.

J. H. BIRKINSHAW.

Effect of repeated contractions of muscle on its lipin content. K. W. BUCHWALD and C. F. CORI (Proc. Soc. Exp. Biol. Med., 1931, 28, 737—740).—The cholesterol, phospholipin, and total fatty acid content of the rat gastrocnemius remained unchanged during prolonged and severe muscular work. In the frog in summer the fatigued muscles of one leg contained 19.7% (dry wt.) less fatty acids than the resting muscles of the other leg.

CHEMICAL ABSTRACTS.

Precursor of ammonia produced in blood and muscle. E. FREUND and B. LUSTIG (Biochem. Z., 1931, 240, 326—327; cf. this vol., 641).—The authors' views concerning the existence of NH_3 in blood and muscle are based on the facts that fresh material deproteinised in the cold gives no brown colour with Nessler's reagent, although 0.1% of added NH_3 gives the colour distinctly, that material which has been kept or has been heated in vac. gives the colour distinctly, and that when the green ppt. given with the reagent is removed a brown colour corresponding in depth with the amounts of NH_3 usually reported is obtained. Hence the criticisms of Parnas (this vol., 1319) are inapplicable.

W. McCARTNEY.

Ammonia production induced by long keeping of frogs' muscles in Barkan solution. G. EMBDEN and M. LEHNARTZ (Z. physiol. Chem., 1931, 201, 273—283).—Prolonged oxybiotic work of frog muscles in Barkan solution induces considerable NH_3 formation, only in part accounted for by deamination of the adenylic acid complex. Unstimulated muscles show a similar behaviour; the O_2 supply has no influence. The effect is probably due to autolytic processes.

J. H. BIRKINSHAW.

Action of bromoacetic acid poisoning on ammonia formation in frog's muscle. G. EMBDEN and L. NORPOTH (Z. physiol. Chem., 1931, 201, 105—132).—In $CH_2Br\cdot CO_2H$ poisoning of frogs after severing the plexus ischiadicus to inhibit the onset of rigor only a small amount of NH_3 is formed in the corresponding gastrocnemius. In normal innerv-

ated muscle a large increase of NH_3 is associated with rigor. Direct and indirect stimulation of muscle after $CH_2Br\cdot CO_2H$ poisoning causes a much greater NH_3 production than in normal muscle. The contraction following fatigue and the gradual death of the muscle after contraction are associated with further NH_3 production. A small number of isolated stimuli causes NH_3 production independent of temp.

J. H. BIRKINSHAW.

Action of bromoacetic acid poisoning on the phosphocreatine metabolism of skeletal muscle. L. NORPOTH (Z. physiol. Chem., 1931, **201**, 133—141).—Considerable hydrolysis of phosphocreatine accompanies $CH_2Br\cdot CO_2H$ rigor. After section of one ischiadicus the innervated muscle long before onset of rigor was richer in phosphocreatine than the control. The action of $CH_2Br\cdot CO_2H$ on the innervated muscle does not cause phosphocreatine hydrolysis.

J. H. BIRKINSHAW.

Influence of protein level on rate of growth in chickens. G. F. HEUSER and L. C. NORRIS (Proc. IV World's Poultry Cong., 1930, 328—342).—Although the wt. after 20 weeks was the same for protein ration levels of 13 and 20%, growth in the first 10 weeks was greater on the 20% level and in the second 10 weeks on the 13% level.

CHEMICAL ABSTRACTS.

Creatine–creatinine metabolism. K. EIMER (Z. ges. exp. Med., 1931, **75**, 428—442; Chem. Zentr., 1931, i, 2898).—Part of the urinary creatinine is probably a metabolic product of chemical processes in the musculature. A. A. ELDRIDGE.

Glycogen in liver cultures. L. DOLJANSKI (Compt. rend. Soc. Biol., 1930, **105**, 504—506; Chem. Zentr., 1931, i, 2898).—Pure cultures of liver cells retain *in vitro* the ability to produce glycogen. The glycogen disappears on rapid growth of the tissue, but again appears when growth is retarded.

A. A. ELDRIDGE.

Metabolism of tartrates. I. Colorimetric determination of tartaric acid. F. P. UNDERHILL, F. I. PETERMAN, and A. G. KRAUSE. **II. Behaviour of tartrate in the organism of the rabbit, dog, rat, and guinea-pig.** F. P. UNDERHILL, C. S. LEONARD, E. G. GROSS, and T. C. JALESKI. **III. Behaviour of tartrates in the human body.** F. P. UNDERHILL, F. I. PETERMAN, T. C. JALESKI, and C. S. LEONARD (J. Pharm. Exp. Ther., 1931, **43**, 357—358, 359—380, 381—398).—II. To the colourless neutral solution to be tested glacial AcOH (1 c.c.) and colourless 5% Na metavanadate solution (4 c.c.) are added and H_2O to 50 c.c. After shaking, the red colour which develops in 10 min. is compared with that in standards similarly treated containing known quantities of tartrate. The method has been adapted for use with urine, blood, grape juice, and baking-powder.

II. When tartrate is administered to rabbit, dog, or cat, either by mouth or parenterally, 90—100% is excreted in the urine. In the case of the guinea-pig, tartrate introduced parenterally is eliminated quantitatively by the kidneys, but introduced by mouth only a small percentage appears in the urine and none in the fæces. It appears, therefore, to be changed in

the intestinal tract of the guinea-pig. Neither in the case of the rabbit nor of the dog does the diet appreciably affect the behaviour of administered tartrate. The rabbit is more susceptible than is the dog to the toxic effects of tartrate on the kidney.

III. In man, tartrate ingested by mouth is excreted in the urine to an extent of less than 20% and none appears in the fæces even after purgative doses. Destruction of the tartrate apparently takes place through bacterial action in the large intestine.

W. O. KERMACK.

Catabolism of fat directly incorporated into the animal body. I. T. BABA (Tôhoku J. Exp. Med., 1931, **17**, 154—167).—Intravenous infusion of a fat emulsion into dogs on a fat-free meat and thyroxine diet quickly lowers the R.Q. (min. 0·707).

CHEMICAL ABSTRACTS.

Blood-phosphorus in fat absorption. B. VAHLQUIST (Biochem. J. 1931, **25**, 1628—1633).—There is a regular increase in the phosphatides of the plasma of dogs after fat ingestion; those of the corpuscles remain practically unchanged. During fat absorption the non-lipoid P of plasma is slightly increased; that of the corpuscles is unaltered. The hypothesis that the fat absorbed from the intestine is transformed into phosphatides of the red corpuscles is therefore not upheld. S. S. ZILVA.

Has the pancreas any influence on the resorption of fat apart from its external lipolytic secretion ? M. NOTHMANN and H. WENDT (Arch. exp. Path. Pharm., 1931, **162**, 472—479).—In depancreatised dogs to which olive oil has been administered by mouth, the total fats in the small intestine consisted of <4% fatty acids, whilst in the large intestine the fatty acids varied from about 14 to 25%. This relatively high figure is probably the result of bacterial action. It is improbable that the pancreas has any effect on the resorption of fat other than through its lipolytic activity.

W. O. KERMACK.

Biochemistry of sulphur. XI. Substitution of dithioethylamine (cystineamine) for cystine in the diet of the white rat. M. X. SULLIVAN, W. C. HESS, and W. H. SEBRELL (U.S. Publ. Health Rep., 1931, **46**, 1294—1301).—A basal diet containing 4% of caseinogen was established on which young male rats gradually gained in wt. Substitution of 0·5% of cystine or cystineamine dihydrochloride for an equal amount of maize starch produced an increased growth rate which was similar up to 6 weeks, but thereafter the latter was effective only to about $\frac{2}{3}$ the extent of the former. P. G. MARSHALL.

Sulphur metabolism of the dog. IX. Synthesis of phenol sulphate and indoxyl sulphate. T. S. HELE (Biochem. J., 1931, **25**, 1736—1744).—Synthesis takes place when the Na_2SO_4 is administered orally or subcutaneously and the PhOH or indole orally. When ethereal sulphate is formed from PhOH or indole at the expense of endogenous S, this S can be replaced at least in part by SO_4''. The ethereal sulphate is formed by the union of SO_4'' with phenolic compounds. S. S. ZILVA.

Presence of phenaceturic acid in the urine of domestic animals. Z. HUBER (Ann. Sci. Univ.

Jassy, 1931, **16**, 497—514).—In dog, cat, rabbit, and poultry the benzene ring is completely destroyed, and in the pig and horse it is partly destroyed. In the ox and sheep it remains intact and is excreted in the urine as hippuric and phenaceturic acids, of which the latter frequently preponderates. H. F. GILLBE.

Effect of fasting and subsequent administration of protein on the formation of mercapturic acid. E. ABDERHALDEN and E. WERTHEIMER (Z. physiol. Chem., 1931, **201**, 267—272; cf. this vol., 868).—Dogs, after fasting 3—5 days, received meat and PhBr. At first mercapturic acid excretion was small or nil, becoming normal only after some days. Cystine fed to a fasting dog gave rise to mercapturic acid in the urine, showing that the power of synthesis was not destroyed. Probably after fasting all the cystine in the first protein supplied is required to replenish the needs of the organism.

J. H. BIRKINSHAW.

Relation of life to electricity. V. Stainability of oil mixtures and white blood-cells by 40 different dyes. R. BEUTNER, J. LOZNER, and B. E. CAYWOOD. **VI. Variation of the electrical resistance of dying tissue as a result of chemical decomposition.** R. BEUTNER, S. H. MANN, and C. M. BLANTON (Protoplasma, 1931, **12**, 481—497, 498—509; cf. this vol., 1084).—V. A dye which is absorbed by a non-aq. mixture containing oleic acid and not by an analogous mixture containing quinine is invariably a nuclear stain. The reverse is the case for cytoplasmic stains.

VI. The electrical conductivity of a non-aq. phase (AcOEt) is largely dependent on its content of fat-sol. acids or bases, highest vals. being obtained with a mixture of acids or bases. In equilibrium with an aq. phase the higher fatty acids produce the greater increase in conductivity, since they are not extracted by H_2O. The initial rise in the resistance of dying or degraded tissue results from the degradation and removal of fatty acids from lipoid cell matter. The later decline in resistance marks the disintegration and dissolution of the cell membranes. Higher conductivity is associated with a more positive p.d. and better basophilic staining in oil mixtures as well as in tissues. A. G. POLLARD.

Buffer values of foods. I. N. KUGELMASS and E. GREENWALD (Amer. J. Dis. Children, 1931, **41**, 1377—1379).—Cereals, fruits, and vegetables have low buffer vals. in comparison with milk, eggs, and meat. Cooked and processed foods have lower buffer vals. than raw foods. CHEMICAL ABSTRACTS.

Biological values of the proteins of breads baked from rye and wheat flours alone or combined with yeast or soya-bean flour. S. K. KON and Z. MARKUZE (Biochem. J., 1931, **25**, 1476—1484).—A supplementary relation exists between the proteins of white wheat flour and those of baker's yeast or of soya-bean flour. There is strong indication that a similar relation exists between the protein of rye flour and of soya-bean flour. The biological val. of the N of crust is lower than that of crumb or of whole bread. S. S. ZILVA.

Deficiencies in rations devoid of roughage for calves. I. Effect of addition of cod-liver oil and lucerne ash. S. W. MEAD and W. M. REGAN (J. Dairy Sci., 1931, **14**, 283—293).—Calves were reared up to 19 months without roughage provided cod-liver oil and lucerne ash were supplied. Without ash the animals were under wt. and the deposition of minerals in the bones was much reduced. Among animals receiving the same ration those showing the greater live wt. had a lower % of ash in the dry fat-free bone. A. G. POLLARD.

Significance of iodine in the energy and metabolic processes of the human body. J. STOKLASA (Z. Ernähr., 1931, **1**, 3—15; Chem. Zentr., 1931, i, 2895).—The effect of soil p_H on the assimilation of I by plants was examined. In plants treated with I the acidity is markedly diminished, particularly in the root system. Ingestion of plants treated with I leads to a diminution of urinary acidity.

A. A. ELDRIDGE.

Calcium assimilation as indicated by bone analysis in long time experiments. A. M. HARTMAN and E. B. MEIGS (J. Dairy Sci., 1931, **14**, 322—336).—The relative proportions of ash, Ca, P, N, and org. matter in cows' bones are little, if at all, altered by long periods of low-Ca rations even when a considerable amount of milk is given in these periods, but the total wt. of bones is reduced by 10—20%. The Ca metabolism in cows receiving a medium quality roughage under natural conditions for long periods is higher than that shown in most balance experiments. A. G. POLLARD.

Dietary factors influencing calcium assimilation. XIV. Influence of mineral acids and sugar on the calcium metabolism of milking cows. E. B. HART, H. STEENBOCK, and O. L. KLINE (J. Dairy Sci., 1931, **14**, 307—321; cf. A., 1930, 636).—Addition of 3 lb. of dextrose to the daily ration had no consistent effect on the Ca assimilation of dairy cows. The daily ingestion of 115 or 230 c.c. of 40% HCl with the ration increased the Ca excreted in the urine and the net Ca loss. A. G. POLLARD.

Calcium and phosphorus balances of milking cows under varying conditions. H. B. ELLENBERGER and J. A. NEWLANDER (Proc. Amer. Soc. Animal Produc., 1928, 25—28).—Liberally milking cows are not always in serious negative Ca and P balance provided they receive adequate grain mixture. Added minerals (steamed bone-meal and limestone) may be assimilated in sufficient quantities to result in positive Ca and P balances.

CHEMICAL ABSTRACTS.

Calcium and phosphorus metabolism. VIII. Influence of thyroid gland and parathyroid hormone on total acid-base metabolism. F. ALBRIGHT, W. BAUER, and J. C. AUB (J. Clin. Invest., 1931, **10**, 187—219).—The thyroid hormone does not act by stimulating the parathyroid glands because it has little effect on serum-Ca and -P. The thyroid does not mobilise Ca phosphate to assist in the excretion of acid metabolites, but exerts a sp. action on Ca-P metabolism. CHEMICAL ABSTRACTS.

Influence of magnesium salts on bone formation and rickets. I. H. VON EULER and M. RYDBOM (Biochem. Z., 1931, **241**, 14—22).—In

experiments with rats, addition of 0·8% Mg to a McCollum diet had an antirachitic action. Similar effects were not obtained with fish (*Gobius niger*) in normal and Mg-free sea-water.

P. W. CLUTTERBUCK.

Modification of the Osborne–Mendel salt mixture. P. B. HAWK and B. L. OSER (Science, 1931, **74**, 369).—The modified mixture for dietary experiments has the same ultimate composition but is easier to prepare.   L. S. THEOBALD.

Chemical sense of the earthworm. O. MANGOLD (Naturwiss., 1931, **19**, 730—735).—Earthworms prefer pure gelatin to gelatin containing quinine, NaCl, or HCl, the discrimination increasing with increased concentration of the admixed compound. They show a slight preference for gelatin containing moderate concentrations of sucrose as compared with pure gelatin. The admixture to pure gelatin of plant material such as the worm commonly eats generally increases preference.   W. O. KERMACK.

Action of pain stimuli on the internal secretions of the adrenals and pancreas, and the blood-sugar. S. A. SCHTSCHERBAKOV, V. S. SIMNITZKI, A. A. VISCHNEVSKI, and S. A. SATVORNIZKAJA (Russ. J. Physiol., 1931, **14**, 152—166).—Faradic stimulation of the ischiadicus in cats and dogs causes an increase of blood-sugar only when the adrenals are intact. When the latter are excluded a decrease in blood-sugar is observed. Blood taken from the vein leaving the adrenal, immediately after the application of the pain-stimulus, increases the blood-sugar of a second animal when injected into the latter. When the pancreas is removed the pain-stimulus causes a sharp increase of blood-sugar of long duration. When both pancreas and adrenals are removed the pain-stimulus does not affect the blood-sugar.

W. O. KERMACK.

Gall-bladder function. II. **Absorption of sodium tetraiodophenolphthalein.** C. G. JOHNSTON (J. Clin. Invest., 1931, **10**, 9—17).—KI is absorbed rapidly and Na tetraiodophenolphthalein more slowly.   CHEMICAL ABSTRACTS.

Absorption and excretion of hexyl- and heptyl-resorcinol under different conditions. B. H. ROBBINS (J. Pharm. Exp. Ther., 1931, **43**, 325—333).—Hexylresorcinol (1 g.) administered to dogs by mouth is excreted in the urine (29%) almost entirely in a conjugated form and in the fæces (67%) in a free state. With larger doses the % excreted in the urine is decreased, but the absolute quantity is increased. The % excreted in the urine is reduced when the compound is given with olive oil or followed by paraffin oil. Hexylresorcinol was never detected in the tissues. In the case of heptylresorcinol about 1% is excreted in the urine and 96% in the fæces.

W. O. KERMACK.

Determination of hexylresorcinol in tissues, blood, and excreta. B. H. ROBBINS and L. G. WESSON (J. Pharm. Exp. Ther., 1931, **43**, 335—337).—The material is extracted with a boiling mixture of 2 vols. of 95% EtOH and 1 vol. of Et_2O. An aliquot portion of the filtered extract is acidified with 2—4 drops of conc. HCl and conc. to $\frac{1}{3}$ vol., diluted with H_2O, extracted with $CHCl_3$, and the extract boiled

with 2 c.c. of 5% aq. NaOH until all the $CHCl_3$ is evaporated. The residue is made up to 2 c.c. with H_2O and the quantity of hexylresorcinol determined colorimetrically following the method of U.S.P., 1926, 323. Heptylresorcinol may be determined similarly.   W. O. KERMACK.

Pharmacology of *d*- and *l*-camphor. III. **Action of the isomerides on the smooth musculature of the leech.** K. A. SCHMELEV (Russ. J. Physiol., 1931, **14**, 249—254).—At concentrations of 1 in 1000, *d*- and *l*-camphor produce at first a stimulating and over longer periods of time a paralysing action in the smooth musculature of the leech. The paralysing action is more marked in the case of *l*- than of *d*-camphor. The stimulating action produced with lower concentrations (1 in 2000 to 1 in 10,000) is the same for both isomerides.   W. O. KERMACK.

Organic bromo-compounds [? bromo-oleic acid]. S. HERMANN and M. FREUND (Klin. Woch., 1931, **10**, 250—253; Chem. Zentr., 1931, i, 2636).—Pharmacologically active compounds are obtained by bromination of triglycerides of unsaturated fatty acids.   A. A. ELDRIDGE.

Lactate concentration in the blood of the rabbit after injection of sodium lactate. I. A. PARFENTIEV, V. D. SUNTZEV, and B. F. SOKOLOV (J. Biol. Chem., 1931, **93**, 797—803).—By enteral or parenteral administration of Na lactate the blood-lactic acid can be raised from the normal level (0·03%) to 0·15—0·17% without danger, whilst a level of 0·20% is lethal. The max. level is attained 1—2 hr. after intravenous and 4—9 hr. after subcutaneous or oral administration. The initial increase is sometimes followed by a decrease to levels below the normal.

F. O. HOWITT.

Percutaneous resorption of alkali salicylates from ointments : determination of salicylic acid in urine. K. W. MERZ (Arch. Pharm., 1931, **269**, 449—456).—Salicylic acid (I) can be detected in the urine of man and rabbit 4 hr. after application of preps. (e.g., lanolin) containing Na, K, or Li salicylate to the skin. Small amounts (0·5—1 mg.) of (I) in urine (10—50 c.c.) are determined by a modification of Sauerland's method (A., 1912, ii, 584).

H. BURTON.

Penetration of certain organic substances through the skin. N. V. LAZAREV, A. J. BRUSSILOVSKAJA, and I. N. LAVROV (Russ. J. Physiol., 1931, **14**, 284—289).—The skin of animals is exposed to the org. substance in question, e.g., C_6H_6 or Et_2O, and the concentration in the expired air is determined by burning it in a suitable electric furnace, absorbing the CO_2 formed in aq. NaOH, and measuring the change of conductivity in the latter.

W. O. KERMACK.

Pharmacological effect of impurities in ether. W. L. MENDENHALL and R. CONNOLLY (J. Pharm. Exp. Ther., 1931, **43**, 315—323).—The cilia of oysters are rapidly paralysed by Et_2O containing small quantities of peroxide or aldehyde, but not by pure Et_2O. This observation may explain the tendency for the development of pneumonia in patients after anæsthesia by impure Et_2O.   W. O. KERMACK.

Toxicity of methyl chloride for laboratory animals. J. L. WHITE and P. P. SOMERS (J. Ind. Hygiene, 1931, **13**, 273—275).—0·0075% of MeCl in air is the min. lethal concentration for guinea-pigs exposed for 72 hr. P. G. MARSHALL.

Effect of general anæsthesia on the nitrogen metabolism. I. II. R. INAMI (Tôhoku J. Exp. Med., 1931, **17**, 39—79, 80—106).—N$_2$O, Et$_2$O, and CHCl$_3$ cause increased destruction of protein in rabbits, as shown by increased urinary N and blood-non-protein-N. The intensity of the anæsthesia is of greater significance than its duration or the quantity of narcotic used. Similar results were obtained with man. CHEMICAL ABSTRACTS.

Pharmacology of local anæsthetics. IV. "Neothesin." H. W. COLES and H. T. ROSE (Anesth. Analg., 1931, **10**, 103—111).—When "neothesin" is injected subcutaneously into the dog, the amount of substance extracted by Et$_2$O from alkaline urine varies with the dose. The acid-titratable substances also increase proportionally. Little unchanged neothesin is excreted in the urine; the blood-non-protein-N, -urea-N, and -dextrose are unchanged. CHEMICAL ABSTRACTS.

Analgesic range of various antipyretics in combination with soporifics. I. Veronal. K. POHLE and W. SPIECKERMANN. **II. Urethane.** K. POHLE and F. VOGEL. **III. Sulphonal.** K. POHLE and P. DITTRICH (Arch. exp. Path. Pharm., 1931, **162**, 685—705, 706—715, 716—726).—I. Pyramidone, quinine, phenacetin, and aspirin were investigated. Combination with veronal in each instance results in some detoxication of the soporific, which is greatest with pyramidone and least with quinine. An increase of analgesic power occurs with phenacetin, aspirin, and quinine, whilst the range is increased in all four combinations. The therapeutic quotient is highest with phenacetin, followed by quinine and aspirin. Commercial veronal–pyramidone preps. are mixtures removed from the optimum.

II. Addition of urethane leads to its detoxication with pyramidone and aspirin, whilst with phenacetin an increase of toxicity occurs over a certain range of mixture. The analgesic power and range of pyramidone, phenacetin, and aspirin are increased, whereas those of quinine are decreased. The combination urethane–pyramidone is therapeutically superior to any urethane-, sulphonal-, or veronal-combination of the 4 antipyretics. No relation between optimum properties and mol. ratio exists.

III. Sulphonal is significantly detoxicated by aspirin and pyramidone, but leads to a decrease in analgesic potency in each instance and to no significant increase in range. F. O. HOWITT.

Hypoglycæmic action of the hypophysectomised dog's blood. R. J. COWLEY (J. Pharm. Exp. Ther., 1931, **43**, 287—293).—When blood from hypophysectomised dogs is injected intravenously into rabbits, a lowering of the blood-sugar of the latter animals takes place, the reduction being more marked than in the case of control animals into which normal dog's blood is injected. W. O. KERMACK.

Mechanism of the hypoglycæmia produced by guanidine and carbon tetrachloride poisoning and its relief by calcium medication. A. S. MINOT (J. Pharm. Exp. Ther., 1931, **43**, 295—313).—In dogs poisoned with CCl$_4$ or with guanidine a marked increase in blood-lactic acid and excretion of lactic acid in the urine is observed as well as a marked hypoglycæmia. These symptoms are inhibited by administration of Ca. In rats guanidine inhibits glycogenolysis by the liver and causes an increased production of lactic acid. The mechanism through which Ca exerts its effect may be associated with adrenaline action, for the effect of Ca, like that of adrenaline, is inhibited by ergotamine tartrate. The close similarity of guanidine and CCl$_4$ poisoning supports the view that the latter compound exerts its action as the result of increasing the guanidine content of the blood. W. O. KERMACK.

Morphine content of the blood and brain after administration of morphine to normal and pre-treated animals. P. FLEISCHMANN (Biochem. Z., 1931, **241**, 233—255).—The blood-morphine content after subcutaneous, intraperitoneal, and intravenous injection of the alkaloid is determined. The morphine concentration is smaller than expected from the dose, reaches a max. after about 1 hr., and then slowly decreases, being detectable after 24 but not after 48 hr. Similar results were obtained with guinea-pigs which had been receiving injections for a long time. The corpuscles contain about twice as much morphine as the serum. In experiments *in vitro* morphine is not destroyed by incubating with blood and its disappearance *in vivo* must be explained by its absorption by the organs. The concentration of morphine in brain is usually lower than in blood. P. W. CLUTTERBUCK.

Santoninamide. K. JOSEPHSON (Svensk farm. Tidskr., 1931, **35**, 69—74; Chem. Zentr., 1931, i, 2885).—*Santoninamide*, C$_{15}$H$_{21}$O$_3$N, m. p. 177—179°, appears not to have the characteristic santonin action on the worm musculature. A. A. ELDRIDGE.

Carbohydrate metabolism of the fatty liver during *Amanita* poisoning. K. IMHÄUSER (Arch. exp. Path. Pharm., 1931, **162**, 506—514).—When the isolated livers of dogs previously poisoned by *Amanita* are perfused, the lactic acid production is much greater than in the case of a normal liver and cannot be completely accounted for by the quantity of glycogen and of lactic acid present in the liver at the beginning of perfusion. The poisoned livers do not appear to be able to resynthesise dextrose from lactic acid. This observation is in harmony with the high lactic acid content of these livers when removed from the animals. The addition of lævulose but not of dextrose to the perfusion fluid increases lactic acid production. W. O. KERMACK.

I. Behaviour of *Digitalis* glucosides in blood and tissue-fluids. II. Penetration of *Digitalis* glucosides into organs. R. A. HOEKSTRA (Arch. exp. Path. Pharm., 1931, **162**, 649—662, 663—684).—I. Digitoxin in Ringer's solution in presence of rabbit-serum at p_H 6·8 or cat-serum does not affect the beat of the isolated frog's heart, whilst in presence of rabbit-serum at p_H 8·3 or with bile and saponin,

frog-serum, heated, enzymically hydrolysed, or inactivated rabbit-serum, the heart ceases to beat. Thus digitoxin combines with the colloids of certain serous fluids, the combination being destroyed at p_H 8·3 or by presence of surface-active substances. Fowl-serum and caseinogen do not quantitatively combine. A similar action is shown by lanogen, but not by other *Digitalis* glucosides.

II. Brilliant-Congo-red or digitoxin in aq. solution does not penetrate a gelatin gel, but does so in presence of sera or peritoneal fluids (cf. A., 1928, 127). Penetration into striated or cardiac muscle-fibres by the drug or dye occurs in presence of serum of the animal from which the muscle was obtained, but not in presence of "foreign" sera or peritoneal fluids except when the muscle is poisoned by EtOH. Sensitisation of the frog's heart against "foreign" proteins does not influence the atoxic combination of digitoxin with these proteins.　　F. O. HOWITT.

Blood-gas content and alkalinity of the arterial blood of rabbits [and dogs] during carbon monoxide poisoning. B. KAMEI (Tôhoku J. Exp. Med., 1931, **17**, 107—126, 127—146).—In rabbits, after subcutaneous injection of CO, the arterial CO_2 decreases. In dogs the CO_2 capacity and the ratio of combined to dissolved CO_2 decrease. $NaHCO_3$ exercises a protective effect.
　　　　　　　　CHEMICAL ABSTRACTS.

Effect of hydrocyanic acid on the respiration of tissue. I. BANGA, L. SCHNEIDER, and A. SZENT-GYÖRGYI (Biochem. Z., 1931, **240**, 454—461).—The respiration of animal tissue in the Barcroft apparatus is only partly inhibited by HCN, and this poison also only partly inhibits the oxidation by tissue of succinic acid. Concentrations of HCN greater than $0·001N$ inhibit the activation of H_2 and hence must not be used when activation of O_2 is being investigated. Since the oxidation of p-phenylenediamine by indophenoloxidase is completely inhibited by HCN the failure of the latter to inhibit the respiration completely cannot be due to incomplete inactivation of the enzyme. It follows either that the activated H_2 is partly autoxidisable or that the O_2 is activated by other substances in addition to indophenoloxidase.
　　　　　　　　W. McCARTNEY.

Effect of arsenious acid on the respiration of tissue. I. BANGA, L. SCHNEIDER, and A. SZENT-GYÖRGYI (Biochem. Z., 1931, **240**, 462—472).—In minced heart muscle two respiratory processes occur. One is inhibited, the other unaffected, by H_3AsO_3. This acid does not affect the activation of O_2, and its inhibitory action has no direct relation to that of HCN. The respiratory power restored to washed muscle by addition of boiled muscle-juice corresponds within certain limits with the respiratory power of unwashed muscle. H_3AsO_3 inhibits the activation of H_2 in the same way as it inhibits the whole respiratory process.　　　　　　W. McCARTNEY.

Biochemical action of arsinic acids of the pyridine series. IV. Isomeric pyridonearsinic acids. A. BINZ and G. WILKE (Biochem. Z., 1931, **241**, 256—259).—A table summarises the toxic and curative doses and the chemotherapeutic indices of the Na_2 salts of 2-pyridone-5-arsinic acid, 3-iodo-2-pyridone-5-arsinic acid, 2-pyridone-3-arsinic acid, 5-iodo-2-pyridone-3-arsinic acid, and 4-pyridone-5-arsinic acid when injected subcutaneously and intravenously into mice and the results are compared with earlier work (cf. A., 1930, 1213).
　　　　　　　　P. W. CLUTTERBUCK.

Ionic migration of bismuth in different bismuth products under different conditions. P. J. HANZLIK and J. B. SPAULDING (Proc. Soc. Exp. Biol. Med., 1931, **28**, 847—850).—Experiments on the treatment of syphilis demonstrated the amphoteric character of Bi. Correlation appeared to exist between cerebral and spinal fluid penetration and the anionic character of Bi.　　CHEMICAL ABSTRACTS.

[Toxicity of] cadmium vapour L. SCHWARZ and W. DECKERT (Zentr. Gewerbehyg. Unfallverhüt., 1931, **18**, 66; Chem. Zentr., 1931, i, 3032).

Effects of overdoses of germanium dioxide on the blood and tissues of rabbits. W. C. HUEPER (Amer. J. Med. Sci., 1931, **181**, 820—830).—Toxic doses of colloidal GeO_2 cause dehydration and increase the oxidative processes of the organism. Excessive doses cause massive brown deposits in various organs. There is a tendency towards alkalosis; variations in blood-sugar are irregular.　　CHEMICAL ABSTRACTS.

Excretion of lead in urine after injection of colloidal lead phosphate. R. K. NEWMAN (Med. J. Austral., 1931, **1**, 373—375).—Injected Pb phosphate is not excreted as such or quickly converted into an excretable form. It is rapidly filtered out of the blood by various tissues which re-liberate excretable Pb into the blood at a fairly const. rate. Colloidal Pb is not eliminated in the same manner as colloidal Pb phosphate.　　CHEMICAL ABSTRACTS.

Intake of lead and its distribution in the organism in experimental poisoning. F. WEYRAUCH (Z. Hyg., 1931, **112**, 559—568).—The resorption of a large proportion of the lead dust (PbS) inhaled by dogs occurs in the intestinal tract and not in the lungs.　　　　　A. G. POLLARD.

Colloid chemistry of the nervous systems. II. W. D. BANCROFT and J. E. RUTZLER, jun. (J. Physical Chem., 1931, **35**, 3036—3057; cf. this vol., 1084, 1088).—The alkali chlorides, bromides, iodides, and thiocyanates can be classified therapeutically as a single group which, in the main, acts by the peptisation of reversibly agglomerated proteins of the nervous systems. K salts should not be used unless the sp. action of $K^{\cdot}$ is desired. NaCNS is comparatively non-toxic. It increases slightly the rate of respiration in men and dogs, but does not disturb the renal function. EtOH in man is definitely antagonised and the NaCNS tends to go to partly agglomerated areas. Large amounts cause vomiting apparently as a result of over-peptisation of the colloids of the centre concerned. NaCNS antagonises "nembutal" and counteracts weak anaphylactic shock. Ephedrine counteracts "Na amytal" anæsthesia better than does NaCNS and is a more powerful peptising agent for albumin.　　L. S. THEOBALD.

Influence of anaphylaxis on blood-sugar variation. I. S. YUN and Y. C. LEE (Trans. Japan. Path. Soc., 1930, **20**, 588—593).—With rabbits, slight hypo-

glycæmia followed injection of normal horse serum. During anaphylaxis hyperglycæmia was observed. The effect of injection of adrenaline, pilocarpine, or insulin is described. CHEMICAL ABSTRACTS.

Enzymic histochemistry. I. Determination of small enzymic fissions. K. LINDERSTRØM-LANG and H. HOLTER (Z. physiol. Chem., 1931, **201**, 9—30).—A method of micro-titration particularly applicable to enzymic hydrolyses is described.
J. H. BIRKINSHAW.

Enzymes of cell respiration. R. KUHN, D. B. HAND, and M. FLORKIN (Naturwiss., 1931, **19**, 771).—The abs. activities of peroxidase, catalase, and respiratory enzymes are approx. of the same order of magnitude. Peroxidase and catalase are partial respiratory enzymes which can be separated and their range of effectiveness circumscribed.
W. R. ANGUS.

Nature of peroxidase. R. KUHN, D. B. HAND, and M. FLORKIN (Z. physiol. Chem., 1931, **201**, 255—266).—The spectrum of reduced peroxidase shows the same bands, 557 and 527 mµ, as reduced hæmin. Proportionality does not exist between the height of the absorption bands of peroxidase solution and peroxidase action. The " hæmin content " of the reduced peroxidase from the spectrophotometric measurements accounts for only about 1/7 of the Fe present. The absorption of peroxidase differs widely from that of catalase except when both are in the reduced state. A slight inhibition of peroxidase is obtained with CO; the product is not reactivated by light.
J. H. BIRKINSHAW.

Peroxidases. Determination of activity. B. B. DEY and M. V. SITHARAMAN (J. Indian Chem. Soc., 1931, **8**, 479—487).—Directions are given for the gravimetric or, better, volumetric determination of the peroxidase in the expressed sap of *Luffa acetangula* by means of the oxidation of conc. benzoquinone solution to quinhydrone in the presence of H_2O_2. The reaction is partly or totally inhibited by dilution.
R. S. CAHN.

Conditions influencing the use of the citric acid enzyme in cucumber seeds for the determination of citric acid. M. ADAMS (Proc. Staff Meetings Mayo Clinic, 1931, **6**, 252).—A H_2O-extract is preferable to the phosphate extract; a H_2O-extract when diluted with phosphate mixture of p_H 6·2—6·7 reduces methylene-blue more slowly than when more alkaline phosphate is used, giving a more definite end-point. The decrease in activity of the dehydrogenase at p_H 6·2—6·7 is small compared with that of interfering substances; the activity was lost at p_H 4·9. With H_2O-extracts at p_H 6·2 a 1 in 5×10^4 solution of methylene-blue can be used; 0·002—0·003 mg. of citric acid can be detected.
CHEMICAL ABSTRACTS.

Structure and enzyme reactions. X. Action of salts on the systems amylase-starch-proteins. H. CHREMPIŃSKA (Biochem. J., 1931, **25**, 1555—1564).—Electrolytes retard the velocity of enzymic hydrolysis of starch. Systems of p_H below the optimal are more sensitive to the action of salts than are those of higher p_H. In the latter case the active concentration of ions is a function of their valency.

The velocity of enzymic hydrolysis in systems containing gelatin is accelerated by the addition of NaCl and retarded by the addition of $CaCl_2$. In systems containing ovalbumin neither heat-coagulation nor $CaCl_2$ affects the velocity of reaction. When egg-white is present heat-coagulation in the presence of $CaCl_2$ accelerates reaction, the velocity depending on the time during which the system is shaken before addition of amylase. NaCl and Na_2SO_4 are without effect in this system. In the absence of $CaCl_2$, heat-coagulation reduces velocity of reaction by 50%. Addition of $CaCl_2$ increases the latter in the presence of dissolved egg-white by about 50%. The same acceleration is obtained by addition of the appropriate quantity of HCl. S. S. ZILVA.

Significance of the Michaelis constant for invertase. G. E. BRIGGS (Biochem. J., 1931, **25**, 1801—1806).—Theoretical. S. S. ZILVA.

Glyoxalase-co-enzyme ratio in liver tissue in inanition. P. VOGT-MØLLER (Biochem. J., 1931, **25**, 1540—1542; cf. this vol., 773).—By using Ariyama's method a considerable loss is observed in the co-enzyme of the liver tissue of starved mice. Dil. solutions of dextrose or of Na nucleate *in vitro* promote methylglyoxal dismutation in co-enzyme-free systems. S. S. ZILVA.

Antiglyoxalase. II. Methods of following glyoxalase action. J. O. GIRŠAVIČIUS (Biochem. J., 1931, **25**, 1807—1814).—Glyoxalase action can be accurately investigated only by determining the acid produced. Manometric methods based on Warburg's glycolytic technique and on the author's method based on the oxidation of glyoxals by H_2O_2 in alkaline solution, are unsuitable. S. S. ZILVA.

Inhibition of glycolysis and disappearance of methylglyoxal. H. K. BARRENSCHEEN, K. BRAUN, and M. DREGUSS (Biochem. Z., 1931, **240**, 381—393).—In materials (blood, liver, kidney, muscle, yeast) in which glycolysis has been inhibited by addition of $CH_2I \cdot CO_2H$ added methylglyoxal disappears (even when pancreas extract containing antiglyoxalase has been added) nearly to the same extent as in those in which glycolysis proceeds undiminished. Most of the keto-aldehyde disappears very quickly after addition, and the disappearance is accelerated if the p_H is shifted to the alkaline side. The disappearance is not due to adsorption, to conversion into pyruvic acid or MeCHO, or to resynthesis of carbohydrate phosphoric esters, although only 48% at most is converted into lactic acid. W. McCARTNEY.

Action of co-enzyme. I. Inhibition of glycolysis and elimination of ammonia. H. K. BARRENSCHEEN and W. FILZ (Biochem. Z., 1931, **240**, 409—422).—When the glycolysis in blood is inhibited by $CH_2I \cdot CO_2H$, $CH_2Br \cdot CO_2H$, NaF; or hæmolysis the amount of NH_3 produced is increased by 300—800% as compared with that produced when glycolysis proceeds undiminished. At the same time a parallel production of the " pyrophosphate fraction " from the co-enzyme occurs and the ratio of NH_3-N eliminated to P liberated is 1 : 1. When glycolysis in hæmolysed blood is produced by addition of phosphate or hydrogen carbonate the production of NH_3 is diminished as

compared with that in the hæmolysed but otherwise untreated blood and the accelerated glycolysis resulting from activation by SO_4'' is accompanied by reduced production of NH_3. It is concluded that the elimination of NH_3 is partly responsible for the inactivation of the co-enzyme, and a scheme illustrating the probable mechanism of the action of the latter, in so far as it is connected with the NH_2-group of the adenylphosphoric acid, is discussed.

W. McCartney.

An enzyme from blow-fly larvæ (*Lucilia sericata*) which digests collagen in alkaline solution. R. P. Hobson (Biochem. J., 1931, 25, 1458—1463).—The excreta of the larvæ, whether sterile or not, contain proteolytic enzymes which digest collagen and elastin, but not keratin. The optimum reaction is at about p_H 8·5. With increasing acidity the activity of the enzyme decreases and almost disappears at p_H 4·0. Collagenase is a distinct enzyme, since it is less stable than the enzymes which act on gelatin and is also adsorbed to a greater extent by charcoal and kaolin.

S. S. Zilva.

Assay of pepsin. H. L. Greenberg (J. Amer. Pharm. Assoc., 1931, 20, 1032—1036).—A modified Sørensen titration method is suggested to replace the official U.S.P. method.

E. H. Sharples.

Heat-inactivation of the proteinase of the pancreas. J. Pace (Biochem. J., 1931, 25, 1485—1490).—Proteinase is adsorbed by kaolin, from which it can be eluted. The heat-inactivation of the proteinase proceeds in agreement with the unimol. formula. Its crit. increment, 35,000—40,000 g.-cal. per molar unit of enzyme, is the same in solutions containing 40, 20, and 0% of glycerol.

S. S. Zilva.

Action of pancreatin on different types of wool. G. Fromageot and A. Porcherel (Compt. rend., 1931, 193, 788—789).—Various samples of sheep's wool subjected to the action of pancreatin at p_H 8·0 at 37—38° undergo a loss in wt., relatively rapid at first, then more gradual, which in a coarse variety may reach 82% of the original wt.

W. O. Kermack.

Nature of the proteases. A. N. Adova and I. A. Smorodinzev (Russ. J. Physiol., 1931, 14, 64—70).—Certain relationships exist between the enzymic activity of protease preps. on the one hand and the surface tension, electrical conductivity, and n of their solutions, the content in N, NH_2- and CO_2H groups and the ratio of the two latter, on the other.

W. O. Kermack.

Proteolytic enzymes. IX. Cleavage of leucyldecarboxyglycine by intestinal erepsin. K. Linderstrøm-Lang (Compt. rend. Lab. Carlsberg, 1931, 19, No. 3, 1—9; cf. this vol., 1190).—The enzyme component present in intestinal erepsin which hydrolyses leucyldecarboxyglycine is not the same as aminopolypeptidase, but may be identical with peptidase II.

J. H. Birkinshaw.

Activity and phosphorus content of aminopolypeptidase. A. K. Balls and F. Köhler (Naturwiss., 1931, 19, 737).—Aminopolypeptidase from pig's intestine freed from accompanying proteolytic enzyme may be purified by precipitation

with $COMe_2$. Highly purified enzyme has a high phosphate content, and this phosphate appears to be intimately related to the enzyme activity. On keeping, the activity decreases and simultaneously PO_4 ions are set free and may be removed by dialysis.

W. O. Kermack.

Action of ultra-violet and visible light on solutions of trypsin, enterokinase, and trypsin-kinase partly or wholly inactivated by heat. J. Pace (Biochem. Z., 1931, 240, 490—493).—Solutions of such enzymes are not reactivated on irradiation with ultra-violet light of wave-length greater than 280 mμ, but, on the contrary, the partly inactivated solutions are further inactivated. The inactivating effect is increased if all the rays from a quartz lamp are allowed to act. Irradiation with visible light has no measurable effect on the activity of the solutions.

W. McCartney.

Presence of urease in the animal organism. S. Majorov (Biochem. Z., 1931, 241, 228—232).—In the dog, the stomach, suprarenals, and ovaries contain, and the pituitary is especially rich in, urease. The mucous membrane of the stomachs of rabbits, pigs, and sheep does not contain urease. Urease of the gastric mucous membrane of dogs is inactivated at 60°.

P. W. Clutterbuck.

Blood-phosphatases. J. Roche (Biochem. J., 1931, 25, 1724—1733).—The phosphatase of the red cells differs from the phosphatases of the bone, kidney, or intestine in its optimum p_H (6·0—6·8) and in its ability to hydrolyse α-glycerophosphate more rapidly than the β-isomeride. The phosphatases of the serum or of the white cells, on the other hand, appear to be identical with bone-phosphatase, as are probably also the kidney- and intestinal phosphatases. Mono- but not di-substituted phosphoric esters are hydrolysed by these enzymes, the rate varying with the nature of the substituting group. The hydrolysis of glycerophosphate by the blood-phosphatases is diminished by the presence of inorg. phosphate or of glycerol. The phosphatases of the serum and red cells synthesise phosphoric esters from inorg. phosphate and various alcohols.

S. S. Zilva.

Phosphatases of mammalian tissues. III. Magnesium and the phosphatase system. H. D. Jenner and H. D. Kay (J. Biol. Chem., 1931, 93, 733—748).—That Mg acts as a sp. activator of dialysed kidney-phosphatase action is confirmed (A., 1928, 671, 1157). Mg will activate all animal tissue phosphatases, including that from bone (cf. A., 1930, 112), either before or, to a greater extent, after dialysis and with α- and β-glycerophosphate, hexosediphosphate, guanine nucleotide, or pyrophosphate as substrate. The optimum concentration of Mg is q_{Mg} 1·7—3·3, where q_{Mg} is the negative log. of molarity of Mg.

F. O. Howitt.

α-Lipase activity of horse serum during the course of multiple bleeding. Z. Gruzewska and G. Roussel (Compt. rend., 1931, 193, 786—787).—Samples of serum obtained from a horse at weekly intervals show a considerable variability, partly seasonal, in their content of α-lipase (enzyme hydrolysing glycerides) as measured by their actions on monobutyrin.

W. O. Kermack.

Direct oxidation of sugar by yeast. K. TRAUT-WEIN and K. WEIGAND (Biochem. Z., 1931, 240, 423—429).—Maltose is directly oxidised by *Saccharomyces Marxianus* and *S. exiguus*, organisms which cannot ferment the sugar. It follows that respiration and fermentation are not necessarily invariably connected. It is probable that sucrose is not directly oxidised by *Schizosacch. octosporus*.

W. McCARTNEY.

Thermal constant and temperature coefficient of fermentation by expressed yeast juice and yeast maceration juice. S. KOSTYTSCHEV and G. MEDVEDEV (Bull. Acad. Sci. U.S.S.R., 1931, 655—660).—Chemical reactions in living cells may be characterised by the high vals. of their heat of activation (thermal const.), $A = \log_e(k_2/k_1) . RT_2T_1/(T_2-T_1)$, and of their temp. coeff. Q_{10} at low temps. For fermentations by expressed and macerated juices from yeast, no thermal const. exists; the vals. of A and Q_{10} for the two juices are very high for the range 1—12° or even for 5—12°. It is concluded that zymase is not a single enzyme and, owing to the regular formation of the same products over the temp. range 1—40°, probably not a simple mixture of different enzymes. T. H. POPE.

Cholesterol, irradiated cholesterol, and alcoholic fermentation with beer yeast. R. DE FAZI and F. PIRRONE (Annali Chim. Appl., 1931, 21, 419—435).—Cholesterol retards alcoholic fermentation of aq. dextrose solutions by beer yeast, but, after exposure in EtOH solution (1%) to the rays of a quartz Hg-vapour lamp, it accelerates the fermentation; the max. effect is obtained when the solution contains 0·05% of cholesterol previously irradiated for 60 min. at 30 cm. from the lamp. Both this accelerating action and the antirachitic effect are regarded as due to substances accompanying the cholesterol. T. H. POPE.

Acyloins. III. Mechanism and kinetics of acyloin formation in fermentation. IV. Non-enzymic acetoin formation and the problem of "carboligase." W. DIRSCHERL (Z. physiol. Chem., 1931, 201, 47—77, 78—104; cf. A., 1930, 893).—III. Fermentation of $AcCO_2H,NaHSO_3$ with dried yeast gave no acetoin, but the latter was produced on addition of MeCHO. In $AcCO_2H$ fermentation the yield of acetoin on the acid fermented steadily increases. For the same CO_2 evolution the acetoin formation is greater with the high concentrations of $AcCO_2H$. Addition of MeCHO increases acetoin formation. The action of heat on dried yeast destroys carboxylase and "carboligase" to the same extent, addition of PhMe inhibits both actions, $CHCl_3$ inhibits chiefly acetoin production, possibly owing to adsorption at the surface of the yeast prep. There is no evidence for the existence of a "carboligase."

IV. Acetoin is produced in quant. yield by irradiation of $AcCO_2H$ in H_2O at M and $0·2M$ concentration. Without solvent or in $COMe_2$ or $CHCl_3$, decarboxylation is slower and the yield of acetoin falls. In abs. EtOH, CO_2 and acetal are produced, but no acetoin. On heating $AcCO_2H$ in a sealed tube or with Os, CO_2 is formed, but no acetoin. Decarboxylation of $AcCO_2H$ with NH_2-acids in boiling H_2O or org.

solvents yields a little acetoin at high concentrations of the acid, except with EtOH, when acetal is formed. A method for determination of acetal and MeCHO when present together is described.

J. H. BIRKINSHAW.

Another co-enzyme of alcoholic fermentation. E. AUHAGEN (Naturwiss., 1931, 19, 916—917).—A study of yeast preps. washed at p_H 7·7—7·8 which could not be activated by the addition of cozymase, Mg, and zymophosphate but were activated by boiled yeast-juice shows that another co-enzyme, cozymase II, is necessary. Boiled yeast-juice ash, adenine, adeninetriphosphoric acid, glutathione, and cysteine cannot be substituted for the boiled yeast-juice. Cozymase II is not destroyed by autolysis of the yeast, is completely destroyed at 100° at p_H 6·0, is precipitated with $Pb(OAc)_2$ and regenerated from the ppt. by H_2S. A. LAWSON.

Effects of cyanide and some other salts on fermentation by yeast preparations. L. M. B. PATTERSON (Biochem. J., 1931, 25, 1593—1607).—KCN (min. concentration 0·006M) slows down the attainment of a max. rate in presence of phosphate without affecting the max. rate attained. The basal rate is lowered. The induction period before the onset of fermentation by zymin, dried yeast, or maceration extract is increased by KCN (min. concentration 0·005M). With yeast-juice (min. concentration 0·075M) it produces an induction period which is otherwise absent. In presence of substances which shorten the induction period of zymin and dried yeast it causes a prolongation to a smaller degree than when acting alone. With yeast-juice in presence of KCN the total acid-sol. P remains const., and there is no change except slight esterification towards the end of the induction period. During the induction period of zymin under various conditions the total and inorg. acid-sol. P increases by the same amount, whilst the org. P remains approx. const. until near the end of that period, when it increases as the inorg. P becomes esterified. In presence of KCN during the first part of the induction period there is a greater increase of acid-sol. inorg. P than of total P, due to hydrolysis of the org. P. The optical rotation and reducing power of the $CCl_3 \cdot CO_2H$ filtrates from the fermentation mixtures show only slight changes until the end of the induction period is approached. In presence of arsenate KCN prolongs the induction period further, but the joint effect is less than the sum of the separate effects. The action of different salts on the induction period is of a different kind. Methylglyoxal shortens the induction period of fermentation with zymin and reduces both the basal rate of fermentation and the rate of esterification. S. S. ZILVA.

Mitogenetic radiation. M. MOISSEJEVA (Biochem. Z., 1931, 241, 1—13).—A table summarises further results. P. W. CLUTTERBUCK.

Production of gluconic acid by moulds. R. SCHREYER (Biochem. Z., 1931, 240, 295—325).—The production of gluconic and other acids from sucrose (in some cases also from dextrose and lævulose) by a large number of moulds (*Aspergillus*, *Penicillium*, *Rhizopus*, *Citromyces*, and others) has been investig-

ated. In almost all cases $H_2C_2O_4$ is found, whilst citric, fumaric, and unidentified acids are occasionally detected. Only some of the moulds certainly produce gluconic acid, others (including all the *Rhizopus* species tested) certainly do not produce detectable amounts, and in some cases the result is doubtful. In the absence of $CaCO_3$ small amounts only of acids accumulate, either because the increasing concentration of acid checks the process, or because continuous decomp. of acid produced takes place, or for both reasons. *P. oxalicum* produces not oxalic but citric acid. *P. corymbiferum* produces material which decomposes $CaCO_3$ without separation of a Ca salt and no malic acid can be detected. All the moulds produce invertase. It is possible that gluconic acid is actually produced in all cases, but in some is at once decomposed. W. McCARTNEY.

Accessory factor necessary for the growth of *Nematospora gossypii*. I. Chemical nature of the factor. II. Relation of the accessory factor to " bios." H. W. BUSTON and B. N. PRAMANIK (Biochem. J., 1931, **25**, 1656—1670, 1671—1673; cf. Farries and Bell, A., 1930, 958).—I. *N. gossypii* is unable to assimilate simple N compounds in synthetic media in the absence of an " accessory factor." This factor is present in association with crude proteins from various sources and in extracts of lentils, etiolated lupin, ox-heart, cotton-leaf, potato, and yeast. It yields two inactive components on precipitation with $Ba(OH)_2$ and EtOH. The active fraction in the "$Ba(OH)_2$ and EtOH ppt." which contains inositol becomes inactive when this compound is removed and active when added again. The activity of some relatively inactive substances is greatly increased by the addition of inositol. The active substance of the fraction not precipitated by $Ba(OH)_2$ and EtOH is precipitated by $Hg(OAc)_2$ and Na_2CO_3.

II. The factor, although associated with " bios " among natural products, is not identical with it. S. S. ZILVA.

Soluble enzymes secreted by *Hymenomycetes*. Comparison of antioxygenic activities of tannin and of the phenolic constituents of essential oils. L. LUTZ (Compt. rend., 1931, **193**, 608—609).—The oxidation of tannin by the oxidase of *Stereum hirsutum*, *S. purpureum*, and *Coriolus versicolor* was not affected by the presence of various phenols, but the oxidation of the latter was in general reduced by the presence of tannin. The antioxidase action of tannin has probably biological significance. W. O. KERMACK.

Importance of zinc for *Aspergillus niger*. M. ROBERG (Zentr. Bakt. Par., 1931, II, **84**, 196—230).— Zn is a necessary nutrient for *A. niger*, but in excess has an inhibitory effect. The organism can utilise Zn in the form of oxide, sulphate, valerate, acetate, and lactate. A. G. POLLARD.

Biochemistry of micro-organisms. XX. Production of mannitol from hexoses and pentoses by a white species of *Aspergillus*. F. P. COYNE and H. RAISTRICK (Biochem. J., 1931, **25**, 1513—1521). —Mannitol was formed by this organism in considerable amounts (15—35% of utilised sugar) from

mannose, galactose, xylose, and arabinose, but not from lævulose, on synthetic media with controlled aëration. The acidity produced was practically negligible in all cases. The results are contrary to those of bacterial fermentation. S. S. ZILVA.

Chemical conditions for growth and zygote formation in *Phycomyces blakesleeanus*. L. RONSDORF (Planta [Z. Wiss. Biol. Abt. E.], 1931, **14**, 482—514).—Zygote formation is not promoted by addition of N to the substrate, but occurs when the sugar : N ratio reaches definite vals. The action of histamine in inducing zygote production is not sp. A. G. POLLARD.

Action of *Aërobacter faeni* on xylose and sucrose. C. R. BREDEN and E. I. FULMER (Iowa State Coll. J. Sci., 1931, **5**, 133—153).—*A. faeni* grows well when NH_4Cl is the sole source of N. The chief products are acetylmethylcarbinol, $\beta\gamma$-butylene glycol, EtOH, HCO_2H, AcOH, butyric, *l*-lactic, and succinic acids, H_2, and CO_2. CHEMICAL ABSTRACTS.

Bacteria belonging to the sub-genus *Aërobacter*. M. GRIMES and A. J. HENNERTY (Sci. Proc. Roy. Dublin Soc., 1931, **20**, 89—97).—With certain specimens of butter a production of gas occurs on incubation with lactose broth for 48 hr. at 21°, but not at 37°. In such cases a typical *Aërobacter* growth is produced on an eosin–methylene-blue medium. Death occurs at 62—70°. Two strains, *A. hibernicum* and *A. liquefaciens*, are described. P. G. MARSHALL.

Decomposition of agar-agar by an aërobic bacterium. S. A. WAKSMAN and W. BAVENDAMM (J. Bact., 1931, **22**, 91—102).—An organism isolated from marine sediments rapidly attacks the hemicellulose complex of agar, utilising it as a source of energy. Much of the C was liberated as CO_2 and a portion used in the production of cell substances. For the latter purpose N is necessary, NO_3' being more effective than NH_4 salts. The organism produces an enzyme which hydrolyses mannan and starch to reducing sugars. A. G. POLLARD.

Inhibition of the acetone–butyl alcohol fermentation by acids. A. M. WYNNE (J. Bact., 1931, **22**, 209—237).—Complete inhibition of the fermentation of maize mash by *C. acetobutylicum* resulted from additions of numerous org. and inorg. acids to produce p_H 3·90—3·65 in the substrate. The effect is associated with a crit. [H˙] within the cell. The greater toxicity of the three chloroacetic acids as compared with AcOH is probably due to the sp. action of the Cl atom and not to [H˙]. Among the lower fatty acids OH-derivatives are more toxic than the normal acids at the same p_H, although possibly the reverse is true of the 3C acids. Pyruvic, lactic, and glyceric acids were tolerated by the organism at higher [H˙] levels than for other acids. In the lower fatty series from HCO_2H to *iso*butyric acid inhibition occurs at practically the same p_H, but there is a steady rise in the crit. p_H in the higher acids up to nonoic. On the basis of molar concentration the inhibitory effectiveness declines from nonoic acid to AcOH. Capillary activity has little effect in the lower acids up to butyric, but has marked influence in the case of higher acids. A. G. POLLARD.

Biochemistry of micro-organisms. XXI. Examination by the carbon balance-sheet method of the types of products formed from dextrose by species of bacteria. J. H. BIRKINSHAW, J. H. V. CHARLES, and P. W. CLUTTERBUCK (Biochem. J., 1931, 25, 1522—1539).—The Czapek–Dox medium as used for the determination of mould metabolism (this vol., 1093) was modified for the cultivation of bacteria. 50 species were found to grow readily on this medium. 20 species were examined by the balance-sheet method at 28° and 34°. The chief classified products were volatile acids, volatile neutral substances, lactic acid, and $\beta\gamma$-butylene glycol. *B. asiaticus-mobilis* gave approx. 30% yield of butylene glycol. S. S. ZILVA.

Factors influencing the production of acetic acid from maize stalks by thermophilic bacteria. C. H. WERKMAN and R. H. CARTER (Proc. Iowa Acad. Sci., 1930, 37, 51—52).—The optimum p_H for acid yield is 9·0, reduction of yield being marked outside the range p_H 8·5—9·5, and the optimum temp. 63°. Grinding the cobs to increase the surface area increased the rate of fermentation and the yield of acid. CHEMICAL ABSTRACTS.

Isomeric forms of lactic acid produced in milk by some of the anaërobes. R. V. HUSSONG and B. W. HAMMER (Iowa State Coll. J. Sci., 1931, 5, 167—170).—When grown on skim-milk, *C. butyricum* produced *i*-lactic acid, whilst *C. Welchii* gave *d*- or *d*-+*i*-lactic acid. CHEMICAL ABSTRACTS.

Optical modifications of lactic acid produced by *Bacterium bulgaricum*. A. KANTARDIEV and I. POPPOV (Milchwirt. Forsch., 1931, 11, 368—370; Chem. Zentr., 1931, i, 2889).—Two strains gave, respectively, in milk *l*-, *l*-; in sugar-bouillon *i*-, *l*-; in wort *l*-, *i*-lactic acid. A. A. ELDRIDGE.

Lactic acid fermentation by *B. acidificans*. Laf. H. SCHRADER (Zentr. Bakt. Par., 1931, II, 84, 1—20).—Volatile acids, notably AcOH and HCO_2H, always accompany the lactic acid produced by *B. acidificans*. The organism, in the presence of CaO, can withstand a temp. of 100° without appreciable effect on its fermentative power. The use of carbonates of Cu, Pb, Ba, or Zn to check fermentation is unsatisfactory. *B. acidificans* cannot transform methylglyoxal, glycerose, or glycerol into lactic acid. Its optimum p_H for acid production is 6·0. A. G. POLLARD.

Action of certain bacteria on uric acid and its derivatives. R. F. HANZAL and E. E. ECKER (Proc. Soc. Exp. Biol. Med., 1931, 28, 815—816).—*Bacterium acidi urici*, Ulpiani, destroyed 30% of the uric acid in 12 hr. and 100% in 24 hr.; *A. aerogenes* destroyed it in 40 hr. at 37°; 1- and 3-methyl-, 1:3- and 3:9-dimethyl-, and 1:3:7-trimethyl-uric acid were not attacked. CHEMICAL ABSTRACTS.

Chemistry of bacteria. I. Lipins of diphtheria bacteria. II. Lipin distribution in acid-fast bacteria. E. CHARGAFF (Z. physiol. Chem., 1931, 201, 191—198, 198—207).—I. Diphtheria bacilli contain 4·9% of material extracted by Et_2O; $CHCl_3$-sol. material is practically absent. The phosphatide (0·41%) contains P 1·42% and N 0·79%,

corresponding with a monoaminomonophosphatide. The $COMe_2$-sol. fat (4%) has acid val. 126·5, sap. val. 176·5, I val. 61·5.

II. The $COMe_2$-sol. fat of the turtle-tubercle bacillus has sap. val. 188·8 and I val. 52·4. It is in part a fatty acid compound of a polysaccharide. No sterols are found. The fats were further subdivided into liquid and solid fractions. The phosphatide has 3·16% P and 0·39% N.

The fat of the smegma bacillus has sap. val. 183·9 and I val. 45·0. The phosphatide has 2·36% P and 0·39% N. No polysaccharide is present. Culture of bacteria on glycerol bouillon appears to increase the $COMe_2$-sol. fat fraction. J. H. BIRKINSHAW.

Variability of tubercle bacilli. IV. Antigenic properties of *S* and *R* cultures. C. E. RICE (Canad. J. Res., 1931, 5, 375—388).—The change from *S* to *R* type in human or bovine tubercle bacilli is accompanied by loss of sp. antigenic activity in the complement fixation reaction. Antisera prepared from *R* organisms lack antibodies against certain substances present in the *S* organisms, but they contain a higher proportion of antibodies reacting with related acid-fast organisms than do the corresponding *S* antisera. W. O. KERMACK.

Fixation of atmospheric nitrogen and formation of ammonia by *Azotobacter*. S. P. KOSTYTSCHEV and SHELOUMOVA (Bull. Acad. Sci. U.S.S.R., 1931, 661—671).—NH_3 is the first identifiable product of the fixation of atm. N_2 by *Azotobacter*; its formation occurs only in presence of energy-providing material. *A. Winelandii* forms NH_3 by destruction of org. N compounds; with glycine and peptone, this process consists of deamination. Such secondary formation of NH_3 is possible only after the complete consumption of the energy-providing material, and hence differs sharply from the primary formation. Each of these reactions takes place only in living cultures. *A. Winelandii* is not killed when kept for 2 days in an O_2-free atm., but in absence of O_2 fixation of atm. N_2 is greatly retarded. T. H. POPE.

Assimilation of molecular nitrogen by micro-organisms. J. BLOM (Zentr. Bakt. Par., 1931, II, 84, 60—86).—In the utilisation of free N_2 by micro-organisms, the initial stage involves the production of NH_2OH brought about by complex Fe-bearing catalysts. This process is adversely affected by the presence of O_2, NH_3, or NO_3'. A. G. POLLARD.

Dimethyl-α-naphthylamine for the determination of bacterial reduction of nitrates. C. H. WERKMAN (Proc. Iowa Acad. Sci., 1930, 37, 53—55).—Dimethyl-α-naphthylamine is superior to α-naphthylamine, but the sensitivity is unchanged; the coloration is permanent and the reagent does not become turbid, the brown discoloration which appears on keeping not interfering with the test. CHEMICAL ABSTRACTS.

Reduction of nitrates by *B. coli*. L. H. STICKLAND (Biochem. J., 1931, 25, 1543—1554).—*B. coli* reduces nitrate completely to nitrite. After PhMe treatment it oxidises formate, lactate, and succinate to CO_2, pyruvate, and fumarate, respectively, by means of nitrate to the same degree as with O_2.

Treatment with PhMe causes a marked change in the p_H-velocity-curve. The variation of the lactate concentration within narrow limits about $0.02M$ causes no great difference in the reaction velocity. The reduction can be completely inhibited by KCN, but not by CO, 50% inhibition being produced by about $0.0001M$-KCN. O_2 causes a non-competitive inhibition of nitrate reduction which is partly removed by CO.   S. S. ZILVA.

Biological decomposition of plant materials. V. Factors determining the quantity of nitrogen immobilised during decomposition. E. H. RICHARDS and A. G. NORMAN. **VI. Effect of [H˙] on the rate of immobilisation of nitrogen by straw.** A. G. NORMAN (Biochem. J., 1931, 25, 1769—1778, 1779—1787).—V. There is no direct relationship between the composition of plant materials and the amount of additional available N immobilised during decomp. (" N factor "). The " N factor " does not represent the whole N active in decomp.; the N of plant-proteins and bacteria may also be utilised. Plant material already containing sufficient or more than sufficient N for decomp. may utilise inorg. N for preference. The N requirements for the decomp. of equal amounts of org. matter (".the nitrogen equivalent ") is an index of the efficiency of the active organisms.

VI. Available N in high dilutions percolating straw filters is immobilised more rapidly under slightly alkaline conditions in the early stages than in either slightly acid or neutral conditions, and ultimately more N is retained. Neutral conditions are more favourable than acid. More org. matter is fermented under alkaline than under neutral conditions and more under neutral than under acid conditions. The alkaline filter shows an initial lag due to the development of a primary flora not very active in cellulose decomp. The loss of hemicelluloses is more gradual in filters than in compost heaps because of the difference in character of the active flora.
                                   S. S. ZILVA.

Bacterial chymases. C. GORINI (Atti Pontif. Accad. Sci., 1929, 83, 66—69; Chem. Zentr., 1931, i, 2629).

Stain for fibrin, Gram-positive bacteria, and basal bodies in tissues. H. M. WALLACE (Science, 1931, 74, 369—370).—Modifications of the Weigert and Gram–Weigert methods for fibrin and Gram-positive bacteria, respectively, are described.
                                   L. S. THEOBALD.

Use of commercial and synthetic maltose in biological research. W. H. SCHOPFER (Helv. Chim. Acta, 1931, 14, 1067—1069).—The development of a fungus (*Phycomyces*), cultivated on a medium containing maltose (I), asparagine, $MgSO_4$, and KH_2PO_4 varies appreciably with the source of (I). Development is much less marked with synthetic (A., 1927, 752) and greatest with Kahlbaum's commercial maltose. It is suggested that a vitamin-*B*-like impurity is present in the last-named variety.
                                   H. BURTON.

Vitamins and the growth of bacteria. F. HODER and A. BREUER (Z. Immunität., 1931, 70, 279—288; Chem. Zentr., 1931, i, 2895).—Active

factors, probably the known vitamins, are present in various fruit and vegetable juices. That present in coconut-milk (" factor Z ") is insol. in fat or Et_2O, and is therefore not vitamin-*A* or -*D*.
                                   A. A. ELDRIDGE.

Appearance and evolution of anti-bodies in horses injected with diphtheria antigens. A. BESSEMANS, G. RAMON, and F. DE POTTER (Ann. Inst. Pasteur, 1931, 47, 358—373).

Bacterial toxins. I. Tetanus toxin. E. MASCHMANN (Z. physiol. Chem., 1931, 201, 219—254). —A toxin prep. was obtained by saturation of the culture fluid (bouillon) with $(NH_4)_2SO_4$. The dry material had about 6 times the activity of the original fluid and was fairly stable. For further purification $Al(OH)_3$ at p_H 6 was the most suitable adsorbent. With kaolin (optimum p_H 3.8) the initial concentration of the aq. spasmin has a large effect; cerebrone and cholesterol were very inefficient. Spasmin is regenerated from the adsorbate with alkaline phosphate solution or 0.05% aq. NH_3, followed by precipitation of the phosphate with MgO mixture or removal of $NH_4˙$ by dialysis. $Al(OH)_3$ and kaolin adsorbates yield the whole of their toxin to serum. The antigenic property of spasmin is present in the adsorbate and is destroyed by treatment of the latter with antitoxin. In the purest prep. the spasmin was present in 210—240 times the original concentration. The mol. does not contain tyrosine, tryptophan, or the group giving the biuret reaction.   J. H. BIRKINSHAW.

Immunological value of anatoxin derived from purified tetanus toxin. S. HOSOYA, M. TAKADA, and S. TERAO (Japan. J. Exp. Med., 1931, 9, 33—38).— The prep. of the purified tetanus toxin (A., 1929, 1109) is described. Subcutaneous injection of the neutralised anatoxin prepared by incubating the toxin with 0.4% CH_2O at 37° for 48 hr. produced no tetany in mice even when the injection corresponded with 5000 min. lethal doses of the toxin. High antitoxic immunity against the purified toxin and tetanus bacilli could be produced (in guinea-pigs) by two injections of the neutral formolised anatoxin.
                                   A. LAWSON.

Cryptotoxins. Phenomenon of the supersaturation of toxins by the salicylic ion. H. VINCENT (Compt. rend., 1931, 193, 620—623).—The complex formed by tetanus toxin and salicylic acid (A., 1928, 674) is very stable, resisting the dissociating effect of $CaCl_2$, $(NH_4)_2SO_4$, or EtOH. When brought to p_H 4.7 by N-HCl, part of the toxin is separated but not destroyed. Toxicity tests carried out with the dialysed solution and the dialysate obtained from the salicylic–tetanus toxin complex, and on the effect of progressive increase of the ratio tetanus toxin/salicylic acid in the incubated complex, indicate that there is a supersaturation of the toxin by the salicylic acid in the original complex, although the part played by the non-toxic proteins may be connected with this result.   A. LAWSON.

Immunisation against toxins and the production of antitoxins. Mixtures of specific antigen and non-specific substances. G. RAMON (Ann. Inst. Pasteur, 1931, 47, 339—357).

Inactivation and reactivation of the virus of herpes. J. R. PERDRAU (Proc. Roy. Soc., 1931, B, **109**, 304—308).—Treatment with O_2 destroyed or reduced the infectivity of 4 out of 13 broth filtrates of this virus. The virus is reactivated by hydrogenation in the presence of colloidal Pd, or by cysteine. The filtrates resistant to O_2 are not sensitised by addition of tyrosinase or sufficient H_2O_2 to neutralise catalase.
A. COHEN.

Effect of bacteriophage on oxidation–reduction potentials of *B. dysenteriæ* **(Shiga) cultures.** L. F. HEWITT (Biochem. J., 1931, **25**, 1447—1451).—The organism possesses feeble reducing powers and resembles in this respect the catalase-containing and not the peroxide-forming bacteria. The bacteriophage itself has no effect on the oxidation–reduction potential, but it inhibits the usual fall in potential of *B. dysenteriæ* cultures by inhibiting the growth and metabolic activation of the bacteria. S. S. ZILVA.

Effect of bacteriophage on the oxidation–reduction potentials of *B. coli communis* **cultures.** L. F. HEWITT (Biochem. J., 1931, **25**, 1641—1646).—The potential of *B. coli* cultures falls to a lower level and much more rapidly, especially in the presence of dextrose, than in the case of other bacteria. In presence of bacteriophage this fall and also the proliferation of the bacteria are delayed, but not inhibited. The effect of bacteriophage on the oxidation–reduction potential follows the effect on the proliferation of the bacteria except that in aërobic dextrose broth cultures of *B. coli* containing bacteriophage there is an initial fall in potential without appreciable bacterial growth. S. S. ZILVA.

Effect of lysozyme on the oxidation–reduction potentials of *M. lysodeikticus* **cultures.** L. F. HEWITT (Biochem. J., 1931, **25**, 1452—1457).—Cultures of this organism contain catalase and do not form peroxide. Growth is more luxuriant and the fall in potential is greater in aërated cultures than in stationary aërobic cultures. The organism contains cytochrome which does not catalyse anaërobic oxidation–reduction reactions. Lysozyme (egg-white or human tears) produces a rapid fall in potential in the cultures followed by a rise before lysis is complete. The older is the culture the slower is the fall and subsequent rise. S. S. ZILVA.

Photodynamic action of certain dyes on the inactivation of *Staphylococcus* **bacteriophage.** C. E. CLIFTON (Proc. Soc. Exp. Biol. Med., 1931, **28**, 745—746).—The bacteriophage was inactivated by incubation with methylene-blue (0·01—0·1%) in presence of both sunlight and air. Cysteine hydrochloride acts as a protective agent. The inactivation is probably due to oxidation of the bacteriophage by photosensitive methylene-blue in presence of O_2.
CHEMICAL ABSTRACTS.

Germicidal activity of essential oils. S. L. MALOWAN (Z. Hyg., 1931, **112**, 93—94; Chem. Zentr., 1931, i, 3479).—The physical behaviour of essential oils (solubility in dil. EtOH) is related to bactericidal activity, aldehydic oils, which are particularly active, being also readily sol. A. A. ELDRIDGE.

Biological action of inorganic compounds. I. Activity of various heavy-metal compounds on bacteria, blood parasites, and experimental mouse cancer. F. KRAUSS and W. A. COLLIER (Arch. exp. Path. Pharm., 1931, **162**, 452—462).—Salts of various heavy metals were inactive against trypanosomes and the spirochætes of relapsing fever. $NiCl_2$, $Cr_2(SO_4)_3$, $PbCO_3$, $PbSO_4$, and $K[Pb_2Cl_5]$ act weakly and $CoSO_4$ and smalt act more strongly on gonococci in the peritoneal cavity of the mouse. $K_2Cr_2O_7$ and K heptanitrosotrithiotetraferriate exhibit marked bactericidal properties *in vitro*. Certain compounds of Cr, Ru, Mn, and Pb are active in experimental mouse cancer. W. O. KERMACK.

Human blood-calcium. IV. G. HETÉNYI and A. VON GAÁL (Z. ges. exp. Med., 1931, **75**, 516—521; Chem. Zentr., 1931, i, 3019).—Adrenaline causes a fall in blood-Ca. A. A. ELDRIDGE.

Sugar exchange of the liver. II. **Free sugar content of liver and variations caused by insulin and adrenaline.** H. MOLITOR and L. POLLAK (Arch. exp. Path. Pharm., 1931, **162**, 488—505).—The true blood-sugar of the liver of fasting rabbits and of dogs has mean vals. of 0·097% and 0·066%, respectively, in both cases lying between 70 and 80% of the normal blood-sugar. The administration of insulin quickly decreases the free sugar of the liver, the fall occurring not later than the fall in blood-sugar. Insulin, therefore, acts directly on the liver, presumably inhibiting glycogenolysis. After the administration of adrenaline the rise in liver-sugar is more marked than that of the blood-sugar. W. O. KERMACK.

Tissue metabolism in pancreatic diabetes and the effect of insulin thereon. H. LASER (Biochem. Z., 1931, **241**, 36—49).—The respiration and lactic acid exchange of the tissue of normal and diabetic hens in hen's serum under physiological pressures of CO_2 with and without addition of insulin are investigated. The respiration is decreased and aërobic lactic acid formation increased in the muscle of the diabetic animal; addition of insulin leads to normal vals.
P. W. CLUTTERBUCK.

Action of insulin on fat metabolism in normal and depancreatised dogs. H. TANGL (Biochem. Z., 1931, **241**, 87—93).—Insulin brings about the conversion of fatty into strongly unsaturated acids, during the disappearance of which the blood-sugar rises. The unsaturated acids are therefore regarded as possible intermediates in the conversion of fat into sugar. P. W. CLUTTERBUCK.

Duodenin, the hypoglycæmic hormone of the intestinal mucous membrane. J. HELLER (Wien. klin. Woch., 1931, **44**, 476; Chem. Zentr., 1931, i, 2894).—An extract of the small intestine of the ox or rabbit reduces alimentary hyperglycæmia or normal blood-sugar; it is also effective when taken orally.
A. A. ELDRIDGE.

Variations in blood-sugar after administration of posterior pituitary extracts. J. LA BARRE (Ar. Int. Pharm. Thér., 1930, **38**, 409; Chem. Zentr., 1931, i, 3136).—Hyper- is followed by hypo-glycæmia; the former is due to increased excretion of adrenaline and the latter to hyperinsulinæmia.
A. A. ELDRIDGE.

Effect of anterior pituitary hormone on the growth and metabolism of the uterus. W.

BÜNGELER and K. EHRHARDT (Klin. Woch., 1931, 10, 593—595; Chem. Zentr., 1931, i, 2632).—In mice considerable glycolysis takes place; it exceeds respiration by 20%. The metabolic change appears to precede the stimulation of growth.
A. A. ELDRIDGE.

Hormones of the anterior pituitary lobe. III. Prolan-A and tumours. IV. Clinical analysis of urine and detection of prolan-A. B. ZONDEK (Klin. Woch., 1930, 9, 679—682, 1207—1209; Chem. Zentr., 1931, i, 3368).—III. Prolan-A is present in the urine in genital carcinoma and sometimes in benign and extragenital malignant tumours.

IV. The urine is slightly acidified with AcOH, treated with 5 vols. of EtOH, and after 24 hr. the ppt. is washed with Et_2O and dissolved in H_2O. The aq. solution contains the hormone. In urine of pregnancy prolan-A and -B are present, but could not be separated with certainty.
A. A. ELDRIDGE.

Oral administration of gonadic extracts to guinea-pigs. H. BEUCHELT (Naturwiss., 1931, 19, 881).—Experiments on wt. increase in mature males and females produced by oral administration of sherry extracts of the gonads of the opposite sex.
P. G. MARSHALL.

Inter-relations between lactic acid and sugar in the blood under the influence of certain hormones. A. I. OSOLIN (Russ. J. Physiol., 1931, 14, 135—151).—" Ovarikrin " has little influence on the carbohydrate metabolism of female rabbits, but its effect is more noticeable on the blood-lactic acid and -sugar of males. Insulin decreases blood-sugar without altering the lactic acid level, whilst adrenaline causes parallel increases in both lactic acid and sugar.
W. O. KERMACK.

Œstrus-producing hormone (menformone). A. Identity of the substance from the urine of pregnant women with that from the urine of pregnant mares. S. E. DE JONGH, S. KOBER, and E. LAQUEUR. B. Crystalline form of the substances. W. NIEUWENKAMP and S. KOBER. C. Absorption spectrum of crystallised menformone samples of different origin. E. DINGEMANSE, S. KOBER, E. H. REERINK, and A. VAN WIJK (Biochem. Z., 1931, 240, 247—262, 263—264, 265—267).—A. Menformone from the urine of pregnant mares (Zondek, this vol., 878) is identical with that from the urine of pregnant women. The œstrus-producing effect in mice and the effect on the undeveloped uterus in rats, on the breasts of male guinea-pigs, and on the genitals of male rats of the two substances is of the same order. Both have the same solubility in org. solvents, the same m. p., and the same optical properties, and both can be distilled in a high vac. The chemical compositions of the substances are the same and their acetates and benzoates are identical. When crude menformone from the urine of pregnant mares is fractionally recryst. from EtOH a *substance*, m. p. 211°, having the same composition as the pure hormone, but only two thirds of its physiological activity, is obtained. This substance may be a mixture containing menformone.

B. Crystallographic examination shows that the substance from the urine of pregnant women has the same form as has that from the urine of pregnant mares and also the theelol described by Slawson (this vol., 790). The menformone crystallised from $CHCl_3$ probably contains solvent of crystallisation and has a form different from that of material crystallised from EtOH.

C. The ultra-violet absorption spectrum of menformone from the urine of pregnant women is identical with that of the menformone from the urine of pregnant mares.
W. MCCARTNEY.

Assay of male sexual hormone in commercial testicular preparations. S. LOEWE, H. E. VOSS, and F. LANGE (Arch. exp. Path. Pharm., 1931, 162, 633—648).—Of 26 preps. tested by the method of cytological regeneration (cf. this vol., 658) 16 were inactive, 9 had a potency of 0·1—0·7, and the remaining sample one of 12·0 mouse units per dose.
F. O. HOWITT.

Action of thyroxine. H. H. MEYER (Ar. Int. Pharm. Thér., 1930, 38, 1—8; Chem. Zentr., 1931, i, 3136).—General physiological and special pharmacological actions of adrenaline are differentiated and discussed.
A. A. ELDRIDGE.

Action of thyroxine on tissue metabolism. A. HOPPING (Proc. Soc. Exp. Biol. Med., 1931, 28, 726—728).—Blood from an alligator which had received an injection of thyroxine had a metabolism 150—100% above the normal; direct addition of thyroxine to the blood produced no change.
CHEMICAL ABSTRACTS.

Influence of the thyroid gland on the regulation of the blood-sugar. V. G. BARANOV (Arkh. Biol. Nauk, 1930, 30, 603—608).—Administration of thyroidin to thyroidectomised dogs does not produce any const. changes in the fasting blood-sugar level. The effect of thyroidectomy on the tolerance curves is counteracted. Thyroidectomy is without effect on the renal threshold for sugar.
CHEMICAL ABSTRACTS.

Influence of the thyroid–parathyroid system and of the sympathetic nervous system on the blood-serum calcium. E. N. SPERANSKA-STEPANOVA (Arkh. Biol. Nauk, 1930, 30, 593—600).—Decerebration of cats caused a brief increase in serum-Ca if the thyroid circulation was left intact. Strong cerebral irritation with simultaneous exclusion of thyroid circulation produced an increase in serum-Ca. Removal or exclusion of the thyroid system may produce prolonged increase in serum-Ca.
CHEMICAL ABSTRACTS.

Suppression of raised basal metabolism during thyroid feeding. I. ABELIN (Naturwiss., 1931, 19, 752—753).—The restriction of the development of hyperthyroidism is studied further (this vol., 865). The amount of di-iodotyrosine administered is important. If too much is given hyperthyroidism may be intensified.
W. R. ANGUS.

Influence of parenteral injection of thyroid gland-cell substance on blood-fat and -lipin. III, IV. S. SAKURAI (Japan. J. Exp. Med., 1931, 9, 1—14, 15—20).—III. The parenteral injection of ox testicle, cow ovary, and ox pancreas emulsions into the rabbit causes in each case a preliminary decrease in blood-cholesterol, lecithin, and total fatty acid, followed by a tendency to increase to original levels

6 hr. after injection. The parenteral injection of ox marrow and suprarenal cortex causes an increase in both cases of blood-cholesterol, lecithin, and total fatty acid, the normal vals. being regained after 6 hr. Injection of an emulsion of ox pituitary causes a slight increase in blood-cholesterol, lecithin, and total fatty acid with a return to original val. after 6 hr. The functions of the internal secretion organs are therefore closely related to the fat and lipin content of the blood, and injection of cell emulsions causes influences resembling hyperfunction of the cells employed.

IV. A summary of previous work is given, from which it is concluded that a close relationship exists between the various organs of internal secretion in their mutual control of metabolism.   A. LAWSON.

Detection of substances with thyroid-like activity in iodoproteins after tryptic digestion or hydrolysis with barium hydroxide. H. MAT-TIS (Arch. Pharm., 1931, **269**, 442—448).—Prolonged tryptic digestion of iodoprotein (6·5% I) gives a sol. product (I) (3·71% I), which has the same action on axolotl as a thyroid prep. Fractionation of (I) by Dakin's BuOH method and assay of (a) the cryst. material separating when the BuOH extract is cooled, (b) BuOH-sol., and (c) BuOH-insol. products show that only (a) is active. Hydrolysis of the iodoprotein with saturated Ba(OH)$_2$ and neutralisation of the hydrolysate with AcOH gives an active product (19·47% I) (similar to that described by Romeis, A., 1923, i, 267), separable by Dakin's method into active (as a) and inactive (as b and c) fractions. These fractions give H$_2$O-sol. and -insol. Cu salts when treated with CuCO$_3$+Cu(OH)$_2$ at 30—35° in vac.
    H. BURTON.

Method of R. Hunt [of thyroid hormone assay]. VI. Dependence of hormone content of the thyroid gland on alimentary and hormonal factors. H. PAAL and W. HUBER (Arch. exp. Path. Pharm., 1931, **162**, 521—536).—The hormone content of thyroid glands of rats on a normal ration as determined by the MeCN-toxicity method (B., 1926, 27) agrees approx. with that of ox-glands (A., 1926, 644). Increase of carbohydrate and protein in the food results in an increase of 100% in the hormone content. Within certain limits the greater is the protein content of the food the greater is the increase in hormone content due to an increment in the carbohydrate intake. Addition of inorg. I to the food produces only a small increase in hormone content, whilst thyroxine, di-iodotyrosine, and similar substances are effective. Injection of insulin inhibits the increase of hormone due to certain diets. Anterior pituitary lobe preps. have an action similar to that of thyroxine. Diets very poor in protein are not always suitable for hyperthyroidism.   F. O. HOWITT.

Results of work on vitamin-A and -D. S. SCHMIDT-NIELSEN and S. SCHMIDT-NIELSEN (Tidsskr. Kjemi Berg., 1931, **11**, 63—68, 84—88).—A review.
    H. F. HARWOOD.

Colour reactions of vitamin-A. M. FABERI and G. SANDICCHI (Arch. Ist. Biochim. Ital., 1931, **3**, 249—262).—An approx. method for the colorimetric determination of vitamin-A by the SbCl$_3$ reaction is described. Vitamin-A in cod-liver oil is destroyed by ultra-violet radiation. The milk of the cow, ewe, or ass contains similar amounts of vitamin-A, which is destroyed by boiling in air or autoclaving. Known constituents of milk do not give the reaction. Human milk contains vitamin-A and the extracted fat gives the SbCl$_3$ reaction even when occurrence of rickets in the child indicates deficiency of vitamin-D
    R. K. CALLOW.

Colour reactions of vitamin-A. K. TAKEDA (Trans. Tottori Soc. Agric. Sci., 1930, **2**, 1—37).—The most trustworthy tests are those employing AsCl$_3$, 1 : 120 SbCl$_5$, kaolin, fuller's earth, and 30% SbCl$_3$.
    CHEMICAL ABSTRACTS.

Highly-concentrated vitamin-A preparations. H. VON EULER and P. KARRER (Helv. Chim. Acta, 1931, **14**, 1040—1044).—The smallest daily dose (per rat) of the highly-purified vitamin-A prep. (I) from *Hippoglossus* (following abstract) causing distinct growth is 0·0005 mg. The activities of different preps. do not parallel their SbCl$_3$ reactions. More active preps. can be obtained from the liver oils from *Scombresox saurus* (II) and *Bothus maxianus* (III). (I) shows absorption max. at 316 and 328 mμ, (II) at 318 and 331 mμ, and (III) at 328—330 mμ.
    H. BURTON.

Vitamin-A from fish oils. P. KARRER, R. MORF, and K. SCHÖPP (Helv. Chim. Acta, 1931, **14**, 1036—1040).—The unsaponifiable matter of the oil extracted from the liver of *Hippoglossus* by low-boiling petroleum is freed from sterols by cooling a solution in MeOH at —15° and —60° and the petrol-eum-sol. residue fractionally adsorbed on fibrous Al$_2$O$_3$. A fraction (I) is thereby obtained as a viscous yellow oil which distils (partly undecomposed) in a high vac., shows a Carr–Price reaction of 10,500 units, and has the characteristic reactions of a carotene derivative. (I) has M 320 (cf. this vol., 771), C 83—84, H 10·5%, contains O, is reduced slowly (with loss in activity) by Al–Hg in Et$_2$O, resists catalytic reduction, and is oxidised by O$_3$ and KMnO$_4$ yielding geronic acid and AcOH, respectively, thus indicating the presence of β-ionone and :CMe·C: groups, respectively. The coloration of (I) with conc. H$_2$SO$_4$ resembles that with dihydrocrocetin and indicates the presence of 6 double linkings. The limiting dose of (I) per day per rat is 0·005 mg.   H. BURTON.

Physiological standardisation of vitamin-A. M. JAVILLIER and L. EMERIQUE (Bull. Soc. Chim. biol., 1931, **13**, 771—778).—See A., 1925, i, 1364.
    C. C. N. VASS.

Effect of artificial drying on the vitamin-A content of alfalfa. S. M. HAUGE and W. AITKEN-HEAD (J. Biol. Chem., 1931, **93**, 657—665).—Artificial drying by hot air or flue-gas preserves the vitamin-A content, whilst field-drying results in a considerable loss due, not to the action of sunlight, but to enzymic activity.   F. O. HOWITT.

Vitamin-B content of vegetables. M. C. HOUSE, P. M. NELSON, and E. S. HABER (Iowa Agric. Exp. Sta. Res. Bull., 1930, No. 120, 335—344).—The cortex of carrot contains more vitamin-B than the xylem and the periderm more than the cortex. Lettuce, kohl-rabi, and tomatoes grown under glass have as

great vitamin-B activity as when grown in direct sunlight. Storage for 5 months did not alter the vitamin-B content of carrots. A. G. POLLARD.

Growth-promoting properties (vitamin-B complex) of the concentrated water-soluble portion of milk. G. C. SUPPLEE, O. J. KAHLENBERG, and G. E. FLANIGAN (J. Biol. Chem., 1931, **93**, 705—725).—Commercial casein is not always freed from vitamin-B_1 and -B_2 by washing with dil. acid. A basal diet supplemented by a limited amount of rice polishings provides sufficient of the vitamins to animals used in the assay of the two factors. The conc. H_2O-sol. fraction of milk after removal of the proteins and most of the lactose is rich in the growth-promoting and antipellagric vitamins, the antineuritic vitamin being present in the least amount. Growth may occur despite wide variations in the amount of rice polishings and H_2O-sol. milk fraction present in the diet. The growth-promoting properties of the concentrate are decreased by autoclaving at 120° for 5 hr. or by ultra-violet irradiation. The necessity for factors other than B_1 and B_2 is indicated. F. O. HOWITT.

Vitamin-B complex of yellow yautiá (*Xanthosoma sagittæfolium*) and of plantain (*Musa paradisica*, L.). J. H. AXTMAYER (Porto Rico J. Pub. Health Trop. Med., 1930, **6**, 229—232).—Vitamin-B_1 is the first limiting factor of the vitamin-B complex of yellow yautiá, and vitamin-B_2 that of plantain. CHEMICAL ABSTRACTS.

Parallelism between phytase and so-called vitamin-B activity in acceleration of development of micro-organisms. C. ARNAUDI (Boll. chim. farm., 1931, **70**, 713—715).—There is complete parallelism between the phytase activity of vitamin-B concentrates and their ability to stimulate the growth of yeast and other micro-organisms, and this extends also to their vitamin-B potency determined by animal tests (cf. this vol., 1098). R. K. CALLOW.

Nutrition. XI. Comparative vitamin-B_1 values of foodstuffs. Fruits and vegetables. R. H. A. PLIMMER, W. H. RAYMOND, and J. LOWNDES (Biochem. J., 1931, **25**, 1788—1800).—Fresh fruits and vegetables have a much lower vitamin-B_1 content than cereals and pulses, but if their high H_2O content is considered the comparison is more favourable. The following are the vals. of the more potent calc. on dry wt. : yeast 100, cereals 10, pulses 13, orange juice 20, orange peel 13, tomatoes 20, cabbage 13, watercress 20, artichokes 9, leeks 10, parsnips 12, and potatoes 12. S. S. ZILVA.

Blood-sugar level in vitamin-B_1 deficiency. M. E. BELL (Biochem. J., 1931, **25**, 1755—1768; cf. A., 1927, 78; 1930, 118).—There is a marked rise in "true sugar" during the convulsive stage in vitamin-B_1-deficient pigeons, but there is no such increase in the case of vitamin-B_1-deficient rats, nor is there a rise in the non-sugar reducing substances or cell vol. of the blood of vitamin-B_1-deficient pigeons or rats. There is usually a fall in blood-sugar in the premortal stages of vitamin-B_1-deficient rats ; on the other hand, pigeons dying from convulsions or from hydropericardium are often hyperglycæmic. Heart-blood from rats killed rapidly has a higher sugar content than the blood taken from the tail of the same animal during life. Different vals. were obtained by various sugar methods with human and pigeon blood. S. S. ZILVA.

Hæmatopoietic function in avitaminosis. VI. Vitamin-B_2 deficiency. B. SURE, M. C. KIK, and M. E. SMITH (Proc. Soc. Exp. Biol. Med., 1931, **28**, 498—499). CHEMICAL ABSTRACTS.

Pathogenesis of avitaminosis-B and its connexion with the lack of certain enzymes in deficient diet. E. CUBONI (Boll. chim. farm., 1931, **70**, 715—717).—Lysocytin is without action on avitaminosis-B. Phytase from rice husk and germ (Belfanti's phosphatase, this vol., 1098) cures polyneuritis in pigeons and, less satisfactorily, in fowls and turkeys. R. K. CALLOW.

Effect of ultra-violet irradiation on the antiscorbutic vitamin of liquid and of dry milk. G. C. SUPPLEE and O. D. DOW (Amer. J. Dis. Children, 1931, **41**, 1353—1362).—Irradiation of dry milk for 3—20 min. under conditions which impart antirachitic properties causes no destruction of vitamin-C ; liquid milk suffers slight loss of vitamin-C. CHEMICAL ABSTRACTS.

Crystalline vitamin-D. F. A. ASKEW, H. M. BRUCE, R. K. CALLOW, J. ST. L. PHILPOT, and T. A. WEBSTER (Nature, 1931, **128**, 758).—When calciferol (this vol., 881) is heated at 180° "pyrocalciferol," an inactive substance of high dextrorotation, is formed. The calciferol previously described probably contained this substance as the main impurity in the 30—50% of inactive material present. *Calciferyl* 3 : 5-*dinitrobenzoate* has m. p. 145—147°, $[\alpha]_{5461}^{20}$ $+104°$ in $COMe_2$, $+68°$ in C_6H_6, and *pyrocalciferyl* 3 : 5-*dinitrobenzoate*, m. p. 167·5—169·5°, $[\alpha]_{5461}^{20}$ $+250°$ in C_6H_6. On hydrolysis these esters give, respectively, calciferol, m. p. 114·5—117°, $[\alpha]_{5461}^{20}$ $+119·5°$, $[\alpha]_{D}^{20}$ $+105°$ in EtOH, $[\alpha]_{5461}^{20}$ $+99°$, $[\alpha]_{D}^{20}$ $+81°$ in $COMe_2$, antirachitic activity 40,000 International units per mg. ; the solution in EtOH has an intense absorption band with a max. ε 46·0 at 265 mμ ; and *pyrocalciferol*, m. p. 92—94°, $[\alpha]_{5461}^{20}$ $+608°$, $[\alpha]_{D}^{20}$ $+494°$ in EtOH, antirachitic activity none ; the solution in EtOH has an absorption band with max. ε 15·7 at 296 mμ, 27·1 at 284 mμ., and 26·1 at 274 mμ.

Calciferol and pyrocalciferol have the same empirical formula as ergosterol. Calciferol is not identical with vitamin-D_1 (this vol., 1098), but closely resembles -D_2 in physical properties. It is a direct product of the irradiation of ergosterol. L. S. THEOBALD.

Crystalline vitamin-D_1. A. WINDAUS, A. LUTTRINGHAUS, and M. DEPPE (Annalen, 1931, **489**, 252—269).—*Vitamin*-D_1, $C_{27}H_{12}O$, m. p. 124—125°, sublimes undecomposed at 135° in high vac., $[\alpha]_{5461}^{20}$ $+171°$ in $COMe_2$ or EtOH (*allophanate*, decomp. about 192°, $[\alpha]_{5461}^{18}$ $+79°$ in $CHCl_3$), is separated from ergosterol irradiated with ultra-violet light in complete absence of O_2 by treatment with citraconic or maleic anhydride, with which it interacts only very slowly (cf. this vol., 840). It shows the reactions of ergosterol, but to a smaller degree, is hydrogenated by Na and EtOH, and absorbs 30 when titrated with BzO_2H, but does not readily absorb O_2 at room temp. The

yield of cryst. product is improved by use of screens to remove light of the shorter wave-lengths (using the Hg-vapour or Mg arc as source).

The isolation of *vitamin*-D_2, m. p. 114—115°, $[\alpha]_D$ +85° in $COMe_2$ (by O. LINSERT), is reported. Both preps. have considerable antirachitic activity, and cause the characteristic poisoning in larger doses.
H. A. PIGGOTT.

Heat of combustion of activated ergosterol. C. E. BILLS, F. G. McDONALD, L. N. BeMILLER, G. E. STEEL, and M. NUSSMEIER (J. Biol. Chem., 1931, 93, 775—785).—Calorimetric, polarimetric, spectrographic, and biological determinations were made on samples of ergosterol and its irradiation product both freshly prepared and exposed to air or CO_2. The ergosterol with $[\alpha]^{20}_{5461}$ −168° in $CHCl_3$ and heat of combustion 9950 g.-cal. had absorption max. at 260, 270, 282, and 293·5 mμ, whilst the fresh resin with $[\alpha]^{20}_{5461}$ +12° in $CHCl_3$, heat of combustion 9931 g.-cal., and a cod-liver oil coeff. of 247,000 had a single broad absorption band at about 270 mμ. Hence the vitamin has no higher energy level and a simple isomeride of the sterol is indicated. Oxidation of the resin results in a marked decrease of heat of combustion, but not of potency, indicating that vitamin-D is not the major part of the resin. Vitamin-D appears to exist in more than one form.
F. O. HOWITT.

Occurrence of vitamin-D in lampreys (*Petromyzontidæ*). R. K. CALLOW and C. F. FISCHMANN (Biochem. J., 1931, 25, 1464—1469).—There is little difference between the antirachitic potencies of oils extracted from the eviscerated body, liver, and ovary of the lampern (*Petromyzon fluviatilis*) and the sea lamprey (*P. marinus*) and from the liver of the lesser spotted dogfish (*Scyllium canicula*). The antirachitic potencies of the livers are much lower than that of the cod. Vitamin-A is also present in these oils.
S. S. ZILVA.

Determination of vitamin-D. Comparison between the preventive and curative methods. P. SCHULTZER (Biochem. J., 1931, 25, 1745—1754).—The preventive is preferable to the curative method. Bone analyses do not give different or more uniform results than those which are obtained by X-ray examination and autopsy.
S. S. ZILVA.

Antirachitic potency of cod-liver oil when mixed and stored in feed 6 and 12 months. L. F. PAYNE (Proc. IV World's Poultry Cong., 1930, 316—322).
CHEMICAL ABSTRACTS.

Fate of the antirachitic factor in the chicken. I. Antirachitic factor balance in the growing chick. D. KLEIN and W. C. RUSSELL (J. Biol. Chem., 1931, 93, 693—704).—Traces of vitamin-D occur in the unsaponifiable fraction from the bodies of unfed newly-hatched chicks and none in that of 4-week chicks fed with irradiated ergosterol or cod-liver oil. During the first 4 weeks of life of chicks fed with either irradiated ergosterol or cod-liver oil of one third the potency of the former the amount of vitamin-D present in the fæces is 26·5 and 43·1%, respectively, of the amount fed.
F. O. HOWITT.

Effect of cod-liver oil and ultra-violet irradiation, as influenced by oyster shell, in the diet of confined laying hens. W. A. HENDRICKS, A. R. LEE, and A. B. GODFREY (J. Agric. Res., 1931, 43, 517—535).—Cod-liver oil is superior to 15 min. daily ultra-violet irradiation. Addition of oyster shell to basal diet increased egg production of hens confined out of direct sunlight and receiving no cod-liver oil.
W. G. EGGLETON.

Effects of the lack of vitamins on the development of teeth. M. SHIBATA (Japan. J. Exp. Med., 1931, 9, 21—32).—The degenerative changes in the histology and chemical composition of the teeth of rats and guinea-pigs fed on diets lacking vitamin-A, -C, and -D and the histological dental changes caused by overfeeding rats on sugar, albumin, fat, and on diets lacking in inorg. salts and nutritive val. are described. Lack of vitamin-B caused no recognisable change.
A. LAWSON.

Hydrogen peroxide as a detector of radiation from organisms. W. STEMPEL (Protoplasma, 1931, 12, 538—548).—Short-wave radiations from the root tips of growing plants are detected by the reduction of H_2O_2.
A. G. POLLARD.

Respiratory oxidation and sugar content in the two sexes of *Mercurialis annua*. R. BOUILLENNE and M. BOUILLENNE (Bull. Acad. roy. Belg., 1931, [v], 17, 980—984).—Male plants of *M. annua* show a larger content of total sugars and of reducing sugars than comparable female plants. This corresponds with the greater respiration observed with male plants.
J. W. SMITH.

Respiration of winter wheat plants at low temperatures. R. NEWTON and J. A. ANDERSON (Canad. J. Res., 1931, 5, 337—354).—The respiration rates of spring and winter wheats were the same when measured at 7°, 0°, or −7° in the autumn. As the plants hardened the rates of respiration decreased, spring wheats showing higher vals. than winter wheats.
A. G. POLLARD.

Chemical changes in nitrogen fractions of plant juice on exposure to frost. R. NEWTON, W. R. BROWN, and J. A. ANDERSON (Canad. J. Res., 1931, 5, 327—332).—Exposure to frost of the expressed juice of unhardened winter wheat plants produced a decrease in coagulable protein content, an increase in NH_2-N, and a greater sensitivity to hydrolysis by dil. NaOH. The inorg. N constituents were unaffected. Addition of sugar to the juice lessened the extent of the changes. Protein cleavage observed in winter-hardened plants is probably the result of frost and is not a protective adaptation.
A. G. POLLARD.

Catalase activity of wheat leaf juice in relation to frost resistance. R. NEWTON and W. R. BROWN (Canad. J. Res., 1931, 5, 333—336).—In winter wheat leaves, the catalase activity of the press juice obtained during late summer and autumn was directly related to the winter hardiness of varieties.
A. G. POLLARD.

Expulsion of gas and liquids from tree trunks. F. W. HAASIS (Science, 1931, 74, 311—312; cf. this vol., 1198).—Trees of *Nyssa sylvatica*, *Quercus rubra*, and *Hicoria glabra* (?) showed a positive gas pressure on insertion of a borer. Those of the latter and of *Castanea dentata* ejected liquid. All trees showing

these phenomena were defective and formed a relatively small proportion of those examined.

L. S. THEOBALD.

Movement of gases into and through plants. P. W. ZIMMERMAN, A. E. HITCHCOCK, and W. CROOKER (Contr. Boyce Thompson Inst., 1931, **3**, 313—320).—Entry of C_2H_4 into plants may occur through stems, petioles, or leaf blades. The gas penetrates the whole plant, even traversing dead sections of tissue. A. G. POLLARD.

Oxygen as an essential factor in wood formation. C. G. SCHWALBE and K. E. NEUMANN (Cellulosechem., 1931, **12**, 287—290).—The juice expressed from birch-wood (cambial layer) has a greater dissolving power for O_2 than either 0·4% aq. dextrose or H_2O. Changes in the sugar content of the juice, and cellulose content and Cl absorption of the wood (after keeping the wood in contact with the juice in presence and absence of O_2), indicate that O_2 is essential for lignification. H. BURTON.

Plant anatomy as conditioned by light intensity and soil moisture. W. T. PENFOUND (Amer. J. Bot., 1931, **18**, 558).—The internal and external structure of plants varied according to the level of moisture maintained in the soil and to the extent of exposure to sunlight. A. G. POLLARD.

Physiology of the seed coat of maize. W. FREYBERG (Bot. Archiv, 1931, **32**, 392—492).—The permeability of the seed coat to various dyes and other solutions is recorded. In general fat-sol. colours dissolved in H_2O containing 30% EtOH penetrated easily. Permeation is dependent primarily on the size of the mols. and is regulated by surface and mol. forces. Results are discussed on the basis of Poiseuille's law. A. G. POLLARD.

Effect of treatments with ethylene chlorohydrin on the p_H of the expressed juice of potato tubers. L. P. MILLER (Contr. Boyce Thompson Inst., 1931, **3**, 321—335).—An increased p_H (0·5—1·0 unit) of the expressed sap of potatoes resulted from treatment of the tubers with the chlorohydrin vapour. The recorded p_H by the H electrode was higher than by the quinhydrone and glass electrodes or by indicators, and increased with the time of passage of H_2 through the liquid. Direct treatment of potato juice with the chlorohydrin caused p_H changes only at very high concentrations and then in an acid direction. Juice from treated potatoes contained more CO_2 than that from controls. The p_H of potatoes increased from the outer surface inwards and the effect of the chlorohydrin was shown by changes in successive layers. Max. change occurred in the intermediate layers 48 hr. after treatment. The effect is not related to the presence of eyes in the tubers and is less in the non-dormant condition. Similar changes are produced by ethylene bromohydrin.

A. G. POLLARD.

Hydrogen-ion concentration of *Digitalis* infusions. J. C. KRANTZ, jun. (Arch. Pharm., 1931, **269**, 470—474).—The p_H of aq. extracts of *Digitalis* decreases slightly with increase in concentration ($c=g$. in 1 litre of extract) of the leaves ; p_H plotted against

log c gives a straight line. The p_H of aq. extracts made from leaves kept for 18 months is slightly lower than the p_H of extracts of fresh leaves.

H. BURTON.

Effect of previous treatment with salt solutions on the subsequent outward diffusion of electrolytes from plant-tissue. C. T. INGOLD (Ann. Bot., 1931, **45**, 709—715).—Pretreatment with the chlorides of Li and Na reduced, and that of K increased, the rate of exmosis of cell electrolytes from plant cells into H_2O. A. G. POLLARD.

Absorption by plants. III. Absorption of potassium in presence of various salts. F. DÍAZ AGUIRRECHE (Anal. Fis. Quím., 1931, **29**, 453—457 ; cf. *ibid.*, 1929, **27**, 368).—When K_2SO_4, K_2CO_3, KNO_3, or K H tartrate are added in increasing quantities the amount of K absorbed reaches a max. which does not change further, whilst the increase in wt. of the plant reaches a sharp max. and then falls rapidly, whilst the P content diminishes slightly.

R. K. CALLOW.

Rôle of phosphorus in the metabolism of plants. E. A. COCKEFAIR (Amer. J. Bot., 1931, **18**, 582—597).—The P content of plants is subject to environmental and hereditary factors. Max. concentrations of P occur at points of max. metabolic activity. Carbohydrate phosphoric esters serve the same purpose in the higher green plants as they do in muscle contraction and in fermentation by yeast.

A. G. POLLARD.

Physiological importance of the mineral elements in plants. III. Distribution of potassium in the potato plant. N. L. PENSTON (Ann. Bot., 1931, **45**, 673—692).—The K content of potato tissue in various stages of growth is determined microscopically, using the cobaltinitrite reagent. All, except dead cork cells, contain K which is localised only in the cytoplasm and vacuole and not in the nucleus and plastids. Accumulations of K are prominent in all actively dividing tissues. Young leaves contain relatively high proportions of K in all green cells, but in yellowing leaves cells of the mesophyll lose K, which accumulates in the vascular bundles prior to translocation. During tuber formation K accumulates in the swollen tips. The distribution of protein is similar to that of K. In parenchymatous cells of the stem, inner cortex, and pith the proportion of protein and K is low and that of starch high. In the tubers starch-forming cells contain abundant K.

A. G. POLLARD.

Influence of heavy-metal compounds on plant cells. A. NIETHAMMER (Protoplasma, 1931, **12**, 554—558).—The rate and extent of the plasmolysis of red-cabbage cells produced by various solutions of $Ni(NO_3)_2$, $Al(NO_3)_3$, Ni K cyanide, and Hg salts are recorded. A. G. POLLARD.

Necessity of boron for health in citrus. A. R. C. HAAS and L. J. KLOTZ (Bot. Gaz., 1931, **92**, 94—100 ; cf. this vol., 1340).—Previous work is extended and confirmed in leaf cuttings and grafted leaf cuttings. The diastatic activity of leaves from B-deficient cultures is slightly higher than from those receiving B.

A. G. POLLARD.