BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

FEBRUARY, 1932.

General, Physical, and Inorganic Chemistry.

General expression for intensity of hydrogen lines. L. McLean (Nature, 1932, 129, 25).
L. S. Theobald.

Supposed anomalous terms of [spectrum of] helium. E. Majorana (Nuovo Cim., 1931, 8, 78—83; Chem. Zentr., 1931, ii, 195—196).—Two new lines ($1s2p^3P_{012}-2p2p^3P_{012}$ and $1s2s^1S_0-2s2s^1S_0$) are recorded. A. A. Eldridge.

Second spark spectrum of boron, B III, in the region 5000—2000 Å. B. Edlén (Z. Physik, 1931, 72, 763—766).—14 new lines in the extreme ultraviolet appeared due to a Li-like system, and from them a term system was deduced for the region 5000—2000 Å. A. B. D. Cassie.

Excitation of the arc spectrum of nitrogen. K. R. More and O. E. Anderson (Physical Rev., 1931, [ii], 38, 1995—1999).—The strong N I lines were as intense as the moderately strong A lines in the arc spectrum of N_2 excited in mixtures of A and N_2. The probable excitation mechanism is discussed.
N. M. Bligh.

New atmospheric oxygen band at 7710 Å. R. Mecke and W. Baumann (Z. Physik, 1931, 73, 139—146).—At great depths of atm. the sun's spectrum shows absorption due to a $^3\Sigma-{}^1\Sigma$ transition of O_2.
A. B. D. Cassie.

Spectra of gases appearing in the early stages of the spark. E. Matuyama (J. Opt. Soc. Amer., 1931, 21, 792—799).—A study of the broadening of the lines due to gases which appear before the electrode spark lines in discharges in air, O_2, and H_2.
N. H. Hartshorne.

Neon–helium bands. M. J. Druyvesteyn (Nature, 1931, 128, 1076—1077).—Two bands, observed near 4000 Å. in the negative glow of Ne–He mixtures, are possibly to be attributed to a compound such as NeHe. L. S. Theobald.

Intensity measurements in the neon column. W. Elenbaas (Z. Physik, 1931, 72, 715—723).—Intensity relations between lines of the principal series were studied for different electric currents, densities of the gas, and cross-sections of the column.
A. B. D. Cassie.

Continuous and "forbidden" series in the sodium arc spectrum. H. Bartels (Z. Physik, 1931, 73, 203—215). A. B. D. Cassie.

***D*-Line fluorescence of sodium at higher pressures.** A. Jabłoński and P. Pringsheim (Z. Physik, 1931, 73, 281—288).—The polarisation of fluorescence *D*-radiation from Na vapour corresponding with 230° was unaffected by magnetic fields up to 80 gauss. A. B. D. Cassie.

Oscillator density for *D*-lines. R. Ladenburg and E. Thiele (Z. Physik, 1931, 72, 697—699).—The number of dispersing electrons per atom effective for the Na *D*-lines is 0·35 and 0·70 for the D_1 and D_2 lines, respectively, and the life of the two resonance levels is $1{\cdot}48\times10^{-8}$ sec. A. B. D. Cassie.

Zeeman effect in quadrupole lines of alkalis. E. Segrè and C. J. Bakker (Z. Physik, 1931, 72, 724—733; cf. A., 1931, 1203).—$^2S-{}^2D$ lines were investigated for Na and K in a magnetic field; the results agree with Rubinowicz's theory of radiation by quadrupoles (cf. A., 1930, 653).
A. B. D. Cassie.

Auto-ionisation in the alkaline-earth metals and the inert gases. H. E. White (Physical Rev., 1931, [ii], 38, 2016—2020).—Certain characteristics of the spectra of Ca, Sr, Ba, Kr, and Xe are explained on the process of auto-ionisation suggested by Shenstone (cf. A., 1931, 1204). N. M. Bligh.

Band spectrum of AsH. G. E. Kimball and J. R. Bates (Nature, 1931, 128, 969).—As contained in the negative electrode of a C. arc in an atm. of H_2 at a potential of 110 volts gave two typical hydride bands, origins at 32,380·2 and 31,636·9 cm.$^{-1}$, and a band probably due to As_2 with the head at 31,802·6 cm.$^{-1}$ The electronic transition is probably of the type $^1\Sigma-{}^1\Sigma$. L. S. Theobald.

Fluorescence of diatomic selenium vapour in the green and yellow regions of the spectrum. J. Genard (Bull. Acad. roy. Belg., 1931, [v], 17, 1235—1240).—The green and yellow fluorescence spectrum of Se_2 vapour excited by the 4047 and 4359 Å. lines from a high-power Hg arc has been investigated spectroscopically. J. W. Smith.

Transmission bands of silver. S. Schubin (Z. Physik, 1931, 73, 273—280).—The broad transmission band of Ag near 3200 Å. is consistent with the quantum-mechanical theory of metals.
A. B. D. Cassie.

Fluorescence of diatomic tellurium vapour excited by mercury lines. J. Genard (Bull. Acad. roy. Belg., 1931, [v], 17, 1241—1248).—The resonance spectrum of Te_2 vapour excited by the Hg lines 4046·7, 4078, 4359, 5461, and 6235 Å. has been investigated. J. W. Smith.

Spark spectra of iodine. L. Bloch and E. Bloch (Ann. Physique, 1931, [x], 16, 503).—Errors in an earlier paper (A., 1929, 617) are corrected.

Nuclear moment of cæsium. W. Schütz (Naturwiss., 1931, **19**, 1007).—An error in the calculation of Barth and Schütz (A., 1931, 1204) is indicated. Corrected vals. for intensity ratio and nuclear moment are 1·41 and 5/2, respectively.
W. R. Angus.

Bands in the spectrum of barium hydride. A. Schaafsma (Nature, 1931, **128**, 1042).—Ba in an atm. of H_2 gave band-heads at 6634, 6689, 6850, and 6923 Å. all shaded towards the violet. The calc. moment of inertia indicates that the bands should be ascribed to BaH. L. S. Theobald.

Arc spectrum of gold. J. C. McLennan and A. B. McLay (Proc. Roy. Soc., 1931, **A**, **134**, 35—41).—The terms of Au I and their vals. based on zero val. for the deepest, $6sS$, are recorded. Classified wave-lengths and intensities are tabulated.
L. L. Bircumshaw.

Hyperfine structure of spectral lines. II. K. Murakawa (Z. Physik, 1931, **73**, 366—375).—The hyperfine structure of Hg I was investigated, and is arranged into hyperfine terms showing nuclear moment zero for the even isotopes, 1/2 for 199, and 3/2 for 201. Every electron in at. nuclei cannot have 1/2 units of spin momentum.
A. B. D. Cassie.

Analysis of the first spark spectrum of mercury. B. Venkatesachar and T. S. Subbaraya (Z. Physik, 1931, **73**, 412—418).—New ^2D and ^4P terms have accounted for 76 HgI lines.
A. B. D. Cassie.

Hyperfine structure of 4916 Å. (Hg I). B. Ventakesachar and L. Sibaiya (Naturwiss., 1931, **19**, 1041—1042). W. R. Angus.

Structure of the mercury line 5461. E. Lau (Ann. Physik, 1931, [v], **12**, 66—68).—With new apparatus the structure of the Hg 5461 line is different from that usually accepted. The structures of the line from a cooled arc and from a discharge tube containing H_2 are compared. A. J. Mee.

Mercury line spectrum in fluorescence. (Lord) Rayleigh (Nature, 1931, **128**, 905).—The lines 3650, 3126, and 2967 Å. are still emitted when Hg vapour is excited by the resonance line alone from a Hg arc. Stepwise absorption thus cannot explain the process by which the vapour is raised to the 3^3D_{321} state. The emission of these lines continues in a rapid stream of vapour even when it has passed out of the region directly illuminated. The results are probably connected with the known ionisation of the vapour by the resonance line.
L. S. Theobald.

Spark spectrum of mercury. J. C. McLennan, A. B. McLay, and M. F. Crawford (Proc. Roy. Soc., 1931, **A**, **134**, 41—47).—A classified list of wave-lengths of Hg II involving many-electron terms is given. L. L. Bircumshaw.

Zeeman effect of a forbidden line. E. Segrè and C. J. Bakker (Nature, 1931, **128**, 1076).—An investigation of the Hg line λ 3680 Å.
L. S. Theobald.

Hyperfine structure of mercury hydride bands. S. Mrozowski (Z. Physik, 1931, **72**, 776—784).—The HgH bands near 4520, 4394, 4219, and 4017 Å. were investigated with crossed Lummer–Gercke plates. A. B. D. Cassie.

Hyperfine structure of spectrum lines of lead arc in the visible and ultra-violet regions. W. Mohammad and P. N. Sharma (Phil. Mag., 1931, [vii], **12**, 1106—1110).—Only the $2s$ level possesses structure; measurements are recorded.
H. J. Emeléus.

Hyperfine structure of spectral lines. K. Murakawa (Z. Physik, 1931, **72**, 793—797).—Hyperfine structure due to Pb I, Pb II, Zn I, Mg I, and Sn I suggests nuclear angular momentum zero for Zn, Mg, Sn, and Pb^{208}, and ½ for Pb^{207}. A. B. D. Cassie.

Wave-length of the green auroral line determined by the interferometer. L. Vegard (Nature, 1932, **129**, 23).—The wave-length found is 5577·340 (or 5)X, in agreement with Babcock's val. of 5577·350 for the green line which appears in night sky luminescence. L. S. Theobald.

Graphical representation of some band [spectroscopical] results. R. Rydberg (Z. Physik, 1931, **73**, 376—385). A. B. D. Cassie.

Nuclear spin and hyperfine structure in band spectra. E. Hulthén (Nature, 1932, **129**, 56—57).—A discussion. L. S. Theobald.

Different kinds of light excitation in the gaseous discharge. E. Lau and O. Reichenheim (Ann. Physik, 1932, [v], **12**, 52—65).—As a result of improvements in the method of observing excitation spectra it has become possible to investigate light emissions which arise from causes other than electron collision. Effects due to the dissociation of H_2 into one excited and one unexcited atom were observed. Light emission due to irradiation was studied, and it was found that the concn. of atoms in the excited, but not metastable, state may be as great as that of the metastable atoms. A. J. Mee.

Spectra of B stars. O. Struve (Astrophys. J., 1931, **74**, 225—267).—Absorption lines for stars of type O9 to B8 are recorded and the elements present given. L. S. Theobald.

Possible explanation of the difference in wave-lengths of the spectral lines of a given element produced on the sun and on the earth. F. Sanford (Science, 1931, **74**, 412—413).
L. S. Theobald.

New mirror spectrometer (monochromator) with single and double dispersion for the region 0·2—4 μ. C. Leiss (Z. Physik, 1931, **72**, 822—828).—A spectrometer of the Wadsworth type is described; the mirrors have a particularly high reflecting power, and the Czerny disposition is used.
A. B. D. Cassie.

Light emission of metallic vapours by excitation in the positive column. H. Krefft (Physikal. Z., 1931, **32**, 948—950).—Certain relationships were found between the light emissions of the alkali metals, connected with their positions in the periodic table. For Cs the recombination spectrum is weakest and it increases with decreasing at. no. The widening of series lines due to the Stark effect is also variable

in the same sense. The results obtained are general for all metal vapours with doublet series.
A. J. Mee.

Emission bands of polar aurora in spectrum of night sky. J. Dufay (Compt. rend., 1931, 193, 1106—1108).—Eight new bands were observed, as well as 13 previously known. The bands may or may not occur in auroral spectra.
C. A Silberrad.

Intensity of interference of rapid cathode rays, and simple interference apparatus for demonstration purposes. F. Kirchner (Physikal. Z., 1931, 32, 969—971).—The different types of electron interference diagrams for thin polycryst. layers and thin single crystals are compared. The angular range for electron reflexion is greater than for *X*-rays, and for very thin layers is considerably greater than the reflexion angle itself. An apparatus suitable for demonstration is described. A. J. Mee.

Angular intensity distribution of continuous *X*-ray spectrum. IV. Stellar opacity coefficient. Y. Sugiura (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 17, 89—110).—Mathematical.
A. J. Mee.

Absolute values of *X*-ray wave-lengths and the fundamental atomic constants. M. Siegbahn and M. Söderman (Nature, 1932, 129, 21—22).—Two methods for fixing the scale of *X*-ray wave-lengths in cm. are described. Definite vals. will be given when exposures under varied conditions with different gratings have been made.
L. S. Theobald.

Structure of soft *X*-ray lines. W. V. Houston (Physical Rev., 1931, [ii], 38, 1797—1801).—The lines produced by the bombardment of a solid target are broader than those emitted by a vapour, as the upper level is not sharp. The line shapes and widths for Be calc. from the free and bound electron models are compared. N. M. Bligh.

Upper atomic-number limits for satellites of the *X*-ray line $L\beta_2$. R. D. Richtmyer (Physical Rev. 1931, [ii], 38, 1802—1807).—The *X*-ray spectral region of the line $L\beta_2$ was investigated photographically for elements of at. no. 50, 51, 52, 53, 56, 58, and 60. The at.-no. ranges of the 5 satellites have, in all but one case, clearly-defined upper limits (approx. at. limit 53). The explanations of previously reported lines beyond these limits are discussed. A new wave-length table is given. N. M. Bligh.

Dependence of the *K*-spectrum of sulphur, excited by *X*-rays, on chemical linking. A. Faessler (Z. Physik, 1931, 72, 734—743).—The $K\alpha$ spectrum of S in compounds was excited by *X*-rays instead of by electron bombardment, and showed former results to be partly due to heat and electrical effects of the electrons; the α-components are displaced to longer wave-lengths in sulphides, and to shorter wave-lengths in sulphates. A. B. D. Cassie.

Determination of atom factors in the region of anomalous dispersion. R. Glocker and K. Schäfer (Z. Physik, 1931, 73, 289—311).—The atom factor of Fe dust between 0·7 and 2·3 Å. changes, not only in abs. val., but also in angular distribution as the *K*-absorption edge is approached. Atom factors were determined for W and Au for wave-lengths longer than the *L*-edge. A. B. D. Cassie.

Field- and photo-effect at outer boundary surfaces. R. Suhrmann (Physikal. Z., 1931, 32, 929—937).—Experiments with photo-cells with very thin layers, sometimes unimol. layers of alkali metals, are described. An explanation of the selective effect is given, and a large effect of field is noted on surfaces emitting electrons. A. J. Mee.

Red displacement of photo-ionisation of alkali atoms on adsorption by negative salt surfaces. J. H. de Boer and M. C. Teves (Z. Physik, 1931, 73, 192—199).—The drop in energy required for photo-emission by alkali atoms on adsorption by salts of negative surface potential is due to formation of negative alkali ions rather than to any conductivity electron effect. A. B. D. Cassie.

Photo-electric and thermionic emission from cobalt. A. B. Cardwell (Physical Rev., 1931, [ii], 38, 2033—2040).—Results on the variation of the photo-electric sensitivity and long-wave limit with extended outgassing, temp. change, and structural alteration, and the effect of the last-named on the thermionic emission, are reported. N. M. Bligh.

Photo-electric properties of tantalum. A. B. Cardwell (Physical Rev., 1931, [ii], 38, 2041—2048). —Experimental. N. M. Bligh.

Determination of the photo-electric threshold for tungsten by Fowler's method. A. H. Warner (Physical Rev., 1931, [ii], 38, 1871—1875).—Photo-current per unit intensity curves for two different W surfaces plotted by Fowler's method (cf. A., 1931, 1106) are in satisfactory agreement with theory.
N. M. Bligh.

Emission of secondary electrons from tungsten. A. J. Ahearn (Physical Rev., 1931, [ii], 38, 1858—1870). N. M. Bligh.

Initiation of ionisation of inert gases by alkali ions. O. Beeck and C. Mouzon (Ann. Physik, 1931, [v], 11, 858—862).—Ionisation, often very sharp, of inert gases by positive alkali ions begins at very different potentials between 70 and 400 volts.
A. B. D. Cassie.

Electron temperatures in inert gases. R. Seeliger and R. Hirchert (Ann. Physik, 1931, [v], 11, 817—857).—Langmuir's electron temp. is definite and reproducible in He, Ne, and A up to pressures of 10 mm.; it falls rapidly with increasing pressure of the gas, and reaches an approx. steady val. between 5 and 10 mm.; it also falls with increasing c.d., this fall being greater the smaller is the gas pressure. At all pressures and currents the electron temp. is greatest in He and least in A. A. B. D. Cassie.

Elastic collisions. J. S. Townsend (Proc. Roy. Soc., 1931, A, 134, 352—356).—Polemical. Criticism by Atkinson with reference to the mean loss of energy of an electron in collisions (A., 1928, 809) and statements of Bullard and Massey with reference to the variation of effective cross-section of atoms with electron velocity (A., 1931, 542) are discussed.
L. L. Bircumshaw.

Electron exchange phenomena in the excited atom. R. Whiddington and J. E. Roberts (Nature, 1931, **128**, 966).—In the case of He no evidence of a transition corresponding with $1S-2S$ singlet or triplet has been obtained (cf. A., 1931, 1107). L. S. Theobald.

Lateral space distribution of *X*-ray photoelectrons. P. Kirkpatrick (Physical Rev., 1931, [ii], 38, 1938—1942).—Results from 752 condensation track photographs for photo-electrons ejected from A by partly polarised *X*-rays of mean wave-length 0·53 Å. are in good agreement with quantum predictions. N. M. Bligh.

Gas concentration of electron radiation. W. Ende (Physikal. Z., 1931, **32**, 942—945).—Experiments described agree in the main with the explanation given by Johnson (J. Opt. Soc. Amer., 1922, **6**, 701) of this phenomenon. A. J. Mee.

Energy loss by medium-velocity electrons in nitrogen and carbon monoxide. E. Rudberg (Ann. Physik, 1931, [v], **11**, 802—816).—Max. in curves of energy loss by electrons of 200—2000 volts when traversing N_2 and CO appear at voltages corresponding with absorption wave-lengths of the optical spectrum; *i.e.*, optical selection rules apply to transitions caused by these electrons. A. B. D. Cassie.

Electron scattering in helium. S. Werner (Proc. Roy. Soc., 1931, **A**, **134**, 202—210).—The scattering of 40—300 volts electrons at a fixed angle of 90° has been measured. The experimental scattering is much greater at low velocities than that calc. from Mott's formula (A., 1930, 974), but agreement is found above 100 volts. L. L. Bircumshaw.

Photo-electrons and negative ions. E. M. Wellish (Proc. Roy. Soc., 1931, **A**, **134**, 427—444; cf. A., 1931, 1347).—The view that during the passage of electrons through a gas some of them become attached to mols., giving rise to negative ions, is shown to be untenable. L. L. Bircumshaw.

Negative ions in hydrogen and water vapour. W. W. Lozier (Physical Rev., 1930, [ii], 36, 1417—1418).—Negative ions have been observed among the positive ions produced in H_2 by electron impact (this vol., 14); their production is confined to a narrow range of electron velocities and is increased by the presence of H_2O vapour. Possible mechanisms of formation are discussed. L. S. Theobald.

Mobilities of atmospheric large ions. R. K. Boylan (Proc. Roy. Irish Acad., 1931, **A**, **40**, 76—85).—Curves were obtained by two methods for air at Dublin. Saturation was not shown at a voltage corresponding with the mobility of the Langevin ion. Ionisation increased by 28—200% at saturation voltage. The existence of large ions of higher and lower mobilities than that of the Langevin ion is indicated. N. M. Bligh.

Production of heavy high-speed ions without the use of high voltages. D. H. Sloan and E. O. Lawrence (Physical Rev., 1931, [ii], 38, 2021—2032).—By successive acceleration in a series of metal tubes synchronised with an oscillating electrical potential, 1,260,000 volt singly-charged Hg ions were produced. N. M. Bligh.

Mobility of positive ions in helium. I. Helium ions. A. M. Tyndall and C. F. Powell (Proc. Roy. Soc., 1931, **A**, **134**, 125—136; cf. A., 1930, 1336).—An improved apparatus is described, by means of which the mobility of positive ions of He in pure He has been found to be 21·4 cm./sec./volt/cm. at 20°/760 mm. The speed of the ions is proportional to E/p, where E is the field in volts/cm. and p the pressure in mm., over a range of E/p from 0·3 to 4·2. L. L. Bircumshaw.

Atoms traversing magnetic fields of varying orientation. P. Güttinger (Z. Physik, 1931, **73**, 169—184). A. B. D. Cassie.

Relative abundance of the chemical elements in white dwarf and its electrification. S. Suzuki (Proc. Imp. Acad. Tokyo, 1931, **7**, 307—310).—The dissociation equilibrium of the various elements in white dwarfs is discussed. W. R. Angus.

At. wt. of fluorine. E. Moles (Nature, 1931, **128**, 966—967).—A crit. discussion of the vals. found by previous investigators. The at. wt. of F, probably, should not exceed 19·000. L. S. Theobald.

At. wt. of xenon. R. Whytlaw-Gray, H. S. Patterson, and W. Cawood (Proc. Roy. Soc., 1931, **A**, **134**, 7—19).—Using a sensitive quartz microbalance, a comparison of the balancing pressures of O_2 and Xe has been made. The ratio was determined for two densities corresponding with pressures of Xe of about 153 and 80 mm., respectively. The at. wt. is found to be 131·26±0·01, in good agreement with Aston's mass-spectrograph val. 131·27±0·04. L. L. Bircumshaw.

Chart of radioactive elements indicating their structure. I. W. D. Hackh (Science, 1931, **74**, 490—492).—The structure of the nucleus and the electron shell of the radioactive isotopes is indicated. L. S. Theobald.

Resonance in atomic disintegration processes. E. Steudel (Naturwiss., 1931, **19**, 1044).—Pose's results on the at. disintegration of Al (cf. A., 1931, 279) could not be verified. W. R. Angus.

Theory of collisions of α-particles and light nuclei. E. Guth and T. Sexl (Physikal. Z., 1931, **32**, 941—942).—Theoretical. In general there is a greater number of scattering phenomena to be expected on the basis of the quantum mechanics theory than on that of classical theory. A. J. Mee.

Range of the α-particles from uranium II. S. Bateson (Canad. J. Res., 1931, **5**, 567—571).—Using a scintillation method the range of the α-particles from U II is 3·29±0·08 cm. at 15° and 760 mm. The experimental procedure and purification of U_3O_8 which was used as source are discussed. The range is in good agreement with the val. of Laurence (A., 1928, 684). The period of U II is shown to be 28,000 years, which is much less than the val. obtained by direct measurement (A., 1931, 891). W. R. Angus.

Interaction energy of two α-particles at close distances, determined from the anomalous scattering in helium. H. M. Taylor (Proc. Roy. Soc., 1931, **A**, **134**, 103—125).—The distance between the centres of two α-particles at which their interaction energy ceases to be that given by the Coulomb law is $3\cdot5\times10^{-13}$ cm. approx. L. L. Bircumshaw.

Anomalous scattering of α-particles by hydrogen and helium. H. M. Taylor (Nature, 1932, **129**, 56).—Calc. and observed vals. for scattering in H_2 and He are in good agreement.

L. S. Theobald.

Scattering of α-particles by light elements. W. Riezler (Proc. Roy. Soc., 1931, **A**, **134**, 154—170).—The scattering of α-particles through large angles by Be, B, C, and Al shows large deviations from that predicted on the assumption of Coulomb forces between the particles, and the deviation increases rapidly with the velocity of the α-particle. The results obtained are predicted by the wave mechanics. An approx. val. is found for the size of the scattering nuclei. L. L. Bircumshaw.

γ-Spectrum of thorium-*C*″ and the Gamow theory of α fine structure. L. Meitner and K. Philipp (Naturwiss., 1931, **19**, 1007).—The two γ-spectrum lines, energies 40·8 and 279 kv., have been detected. The results contradict the Gamow theory of α fine structure. W. R. Angus.

Monochromatic de Broglie molecular ray waves. I. Estermann, R. Frisch, and O. Stern (Z. Physik, 1931, **73**, 348—365).—De Broglie waves due to mol. rays were rendered monochromatic by two methods: reflexion at a LiF crystal surface, and by selection of rays of one velocity by a rotating toothed wheel. The wave-length was in each case measured by reflexion at a second LiF crystal surface.

A. B. D. Cassie.

Appearance of spatial quantisation. T. E. Phipps and O. Stern (Z. Physik, 1931, **73**, 185—191).

A. B. D. Cassie.

Triatomic or monatomic hydrogen. G. R. Schultze (J. Physical Chem., 1931, **35**, 3186—3188; cf. A., 1931, 805).—The characteristics of activated H do not necessarily point to the presence of H_3; another explanation of the activity is possible (cf. *ibid.*, 440). C. T. Snell (*c*).

Experimental proof of the spin of the photon. (Sir) C. V. Raman and S. Bhagavantam (Indian J. Physics, 1931, **6**, 353—366).—The depolarisation observed with light scattered by gases or liquids is more closely in accord with that anticipated on the spinning photon theory than on the classical theory.

J. W. Smith.

Collision problems involving large interactions. O. K. Rice (Physical Rev., 1931, [ii], **38**, 1943—1960).—Mathematical. N. M. Bligh.

Evaluation of the matrix components for helium. L. P. Smith (Physical Rev., 1931, [ii], **38**, 1961—1968).—Mathematical. N. M. Bligh.

Structure of the nucleus and its total moment of momentum. S. D. Bryden, jun. (Physical Rev., 1931, [ii], **38**, 1989—1994).—Theoretical.

N. M. Bligh.

Mass of the proton. (Sir) A. Eddington (Proc. Roy. Soc., 1931, **A**, **134**, 524—532).—Mathematical. By a development of the geometrical theory the mass of the proton as well as that of the electron can be calc. from the recession of the spiral nebulæ.

L. L. Bircumshaw.

Ultra-violet absorption of aqueous solutions of chlorides. R. Tréhin (Compt. rend., 1931, **193**, 1089—1091; cf. A., 1931, 19).—The absorption spectra of NaCl, KCl, LiCl, $BaCl_2$, and $SrCl_2$ between λ 2816 and 1990 Å. are similar, but different from that of HCl save in very dil. solution. In more conc. solutions the metallic cations in association with H_2O and Cl^- modify the absorption differently from H^+. Sufficiently conc. solutions of LiCl show a max. absorption. C. A. Silberrad.

Optical investigation of perylene and its derivatives. III. Ultra-violet absorption spectrum. H. Conrad-Billroth (Z. physikal. Chem., 1931, **B**, **15**, 1—17; cf. A., 1929, 487).—The ultra-violet absorption spectra of perylene and 11 derivatives consist of two groups of bands, one of which is to be ascribed to the benzenoid linking and the other to the linking between two rings. The optical data have thus made it possible to derive electronic formulæ for the three quinones examined. From the spacing of the perylene bands nuclear frequencies of 1330, 920, and 300 cm.$^{-1}$ are deduced, and by means of these vals. it has been possible to obtain an equation giving the max. in the spectrum of the hydrocarbon, and, with different coeffs., the max. in the spectra of its derivatives. R. Cuthill.

Normal vibrations of carbonate and nitrate ions. A. C. Menzies (Proc. Roy. Soc., 1931, **A**, **134**, 265—277).—Dennison's method (A., 1926, 222) has been used to calculate the frequencies of the normal modes of vibration of the CO_3 and NO_3 ions. A characteristic equation is obtained differing from Nielsen's. The consts. in the formulæ have been calc. from infra-red and Raman effect data for calcite and $NaNO_3$. The magnitude of the binding forces between the central and outer atoms suggests that they are appropriate to the second excited state of CO and NO, respectively. L. L. Bircumshaw.

Vibrations of pentatomic tetrahedral molecules. H. C. Urey and C. A. Bradley, jun. (Physical Rev., 1931, [ii], **38**, 1969—1978).—Andrews' suggestion (cf. A., 1930, 1345) for the choice of restoring forces along and perpendicular to the chemical linkings is tested. The agreement of calc. and observed vals. of vibrational frequencies with this choice of forces is unsatisfactory. A correction for repulsive forces between corner atoms secures better agreement.

N. M. Bligh.

Emission spectrum of carbon dioxide. H. D. Smyth (Physical Rev., 1931, [ii], **38**, 2000—2015).—Complete data for the range 6500—1400 Å. and a partial analysis are reported. N. M. Bligh.

Faint branches in the OH bands. G. M. Almy and G. D. Rahrer (Physical Rev., 1931, [ii], **38**, 1816—1817; cf. A., 1930, 1074).—Weak branches detected photographically are identified by comparison of observed and calc. wave nos.

N. M. Bligh.

Far infra-red. J. Strong (Physical Rev., 1931, [ii], **38**, 1818—1826).—Using a new instrument (cf.

A., 1931, 996) for the range 20—150 μ, data are reported for reflectivities of rough surfaces, galena, β-magnesia, zincite, stibnite, corundum, sphalerite, molybdenite, and cuprite, transmissivities of KBr, KI, a layer of KCl evaporated on a lacquer film, a thin film of amorphous quartz, liquid CCl_4, and powdered Al and Cu, and emission of liquid and solid NaCl near the m. p. N. M. Bligh.

Infra-red spectrum and the molecular configuration of N_2O. E. K. Plyler and E. F. Barker (Physical Rev., 1931, [ii], 38, 1827—1836).—Data for the vibration spectrum and rotational analysis are given. The non-symmetrical linear mol. form N⋮N:O is indicated. The single Raman line 1281 cm.$^{-1}$ is observed. N. M. Bligh.

Infra-red absorption bands of hydrogen cyanide in gas and liquid. F. S. Brackett and U. Liddel (Smithsonian Misc. Coll., 1931, 85, No. 5, 1—8).—Of the 15 bands observed for the liquid between 1 and 2 μ, 14 are combinations or harmonics of the fundamentals proposed by Badger and Binder (A., 1931, 667). With the saturated vapour at 22·5° the bands $2\nu_1$, $3\nu_1$, and $2\nu_1+\nu_2$ were observed as doublets, no *Q* branch being present. Badger and Binder's val. of moment of inertia, and their conclusions regarding arrangement of atoms etc., are confirmed. Chemical Abstracts.

Infra-red radiation of the terrestrial atmosphere. J. Devaux (Compt. rend., 1931, 193, 1207—1209).—Using a specially designed spectrograph with rock-salt prisms and a radiomicrometer, radiation of the zenith sky has been compared with that of a black body at known temp. A wide band at 8—14 μ and a narrow one at 5 μ are attributed to H_2O and perhaps CO_2; a small secondary max. at 10 μ is probably due to O_3 at a moderate temp.

C. A. Silberrad.

Laminary reflexion gratings for infra-red investigation. C. H. Cartwright (J. Opt. Soc. Amer., 1931, 21, 785—791).—The intensity distributions of laminary reflexion gratings are given, and several methods of making them and a new method of making an echelette grating are described.

N. H. Hartshorne.

Molecular scattering of light. (Sir) C. V. Raman (Indian J. Physics, 1931, 6, 263—273).—Nobel lecture. J. W. Smith.

Circular polarisation of Raman lines. A. Kastler (Compt. rend., 1931, 193, 1075—1078).—The fact that the Raman lines produced by circularly polarised light, when viewed longitudinally, are inversely polarised, and when viewed transversely depolarised (cf. A., 1931, 668, 997), implies theoretically that *Q* lines should behave in reverse, *P* and *R* lines in similar fashion. This is in accordance with the selection rules for the Raman lines, which require that $\Delta=0$ (*Q* lines) or ±2 (*P* and *R* lines), the privileged direction being that of the polarisation of the incident beam (cf. this vol., 107).

C. A. Silberrad.

Circular polarisation of Raman lines. A. Cotton (Compt. rend., 1931, 193, 1078—1079).—The effect on the Raman lines produced in $PhNO_2$ by the indigo line of Hg, of a magnetic field of 48,300 gauss normal to both incident and diffused beams, is to increase the intensity of the lines 1112, 1342, and 1587 cm.$^{-1}$ when vibrations are parallel to the field, and of 1112 and 1587 when normal thereto. The diffused line (4916 and 5461) are unaffected.

C. A. Silberrad.

Relative intensities of Stokes and anti-Stokes lines in the Raman spectrum. S. C. Sirkar (Indian J. Physics, 1931, 6, 295—303).—The ratio of the intensities of the Raman lines of frequencies $\nu+\nu_{mn}$ and $\nu-\nu_{mn}$ in the case of the two CCl_4 lines $\nu_{mn}=1368\times10^{10}$ and 945×10^{10} respectively is represented more accurately by the expression $\{(\nu+\nu_{mn})/(\nu-\nu_{mn})\}^4\cdot e^{-h\nu_{mn}/kT}$ as given by Placzek's theory than by the Boltzmann factor alone.

J. W. Smith.

Raman effect in gases. I. Experimental results. II. Theoretical considerations. S. Bhagavantam (Indian J. Physics, 1931, 6, 319—330, 331—344).—The Raman effect in H_2, O_2, N_2, CO_2, N_2O, C_2H_2, H_2S, and SO_2 has been studied at pressures up to 50 atm. The frequencies are in good agreement with those reported by previous authors. Lines representing vibrational transitions are usually well polarised, whereas those from rotational transitions are imperfectly polarised. Above a certain pressure the fine structure disappears. This crit. pressure corresponds with the state where the frequency of mol. rotation is the one quantum state.

II. The theory of Raman scattering, both rotational and vibrational types, is discussed, and comparison is made between theory and observation for the intensity and polarisation of light scattered by diat. mols. J. W. Smith.

New Raman bands of water. E. Segrè (Atti R. Accad. Lincei, 1931, [vi], 13, 929—931).—In the Raman spectrum of H_2O excited by the 2537 Å. Hg line a band with a max. at 140 cm.$^{-1}$ has been found. It is attributed to oscillations in polymerised H_2O mols. O. J. Walker.

Raman band of water. G. Bolla (Nature, 1932, 129, 60).—The reported peculiarity of the Raman band of H_2O (A., 1931, 1353) may be produced or essentially modified by interference in the spectrograph used. L. S. Theobald.

Raman spectra of some inorganic chlorides. S. Venkateswaran (Indian J. Physics, 1931, 6, 275—285).—The Raman spectra of SO_2Cl_2, S_2Cl_2, PCl_3, $POCl_3$, and BCl_3 have been studied, and the structures of these mols. are discussed. The frequency 1290 cm.$^{-1}$ is attributed to P:O. J. W. Smith.

Raman spectrum of ammonia in solution at various concentrations. V. Ricca (Atti R. Accad. Lincei, 1931, [vi], 14, 197—200).—Aq. solutions of NH_4 salts do not show any Raman lines which can be attributed to NH_4^+. Aq. solutions of NH_3 give a Raman spectrum identical with that of liquid NH_3. So far no lines characteristic of NH_4OH have been found. O. J. Walker.

Circular polarisation of Raman lines. W. Hanle (Ann. Physik, 1931, [v], 11, 885—904).—Polarisation of Raman radiation due to a circularly polarised primary was investigated for CCl_4, $CHCl_3$, C_6H_6, PhMe, MeOH, EtOH, and $CH_2Pr^{\beta}\cdot CH_2\cdot OH$; corresponding vibrations in different substances show the same circular polarisation. A. B. D. Cassie.

Raman effect and chemical constitution: the *cyclo*propane nucleus. R. Lespieau, M. Bourguel, and R. Wakemann (Compt. rend., 1931, **193**, 1087—1089).—*cyclo*Propane has Raman lines at 1188, 3011, and 3028 $cm.^{-1}$ and bands with centres at 867, 1439, and 3076, disagreeing with Yates' (cf. A., 1931, 545) but in fair agreement with Bhagavantam's (cf. A., 1930, 1237) calculations. Comparison with the Raman spectra of its Me, Me_2, Me Et, Me Pr, Ph, and Ph_2 derivatives shows that the C·C linking in the C_3 nucleus is characterised by a strong line near 1188 (1208, 1214, 1209 and 1221, 1207 and 1221, 1221, 1227, respectively), increasing in frequency with increased mol. wt., and is a doublet when there are two different substituents. The C·H linking is characterised by a line, or pair of lines, between 2999 and 3028, and a band between 3061 and 3076, resembling the ethylenic spectrum. C. A. Silberrad.

Raman effect and nature of allenic linkings. M. Bourguel and L. Piaux (Compt. rend., 1931, **193**, 1333—1335).—The Raman spectrum of allene gives no indication of lines or bands characteristic of either double or triple linkings (cf. A., 1930, 978; this vol., 7); it consists of strong lines at 1074 and 3000, and indistinct bands at 1440 and 3073. Propyl-, butyl-, and αα-dimethyl-allenes give similar results, the changes accompanying substitution being similar to those in the *cyclo*propanes (cf. preceding abstract). It is concluded that the linkings in allene cannot be "ethylenic." C. A. Silberrad.

Raman spectrum of formic acid. S. Parthasarathy (Indian J. Physics, 1931, **6**, 287—293).—A crit. study has been made of the Raman spectrum of HCO_2H. The characteristic frequencies and the effects on these of heating, addition of H_2O, and polarisation are described. J. W. Smith.

Raman spectra of some organic crystals and solutions. P. Krishnamurti (Indian J. Physics, 1931, **6**, 309—317).—The Raman spectra of NH_4OAc, $Cd(OAc)_2$, $Zn(OAc)_2$, $Pb(OAc)_2$, $H_2C_2O_4$, $(NH_4)_2C_2O_4$, C_2Cl_6, $CO(NH_2)_2$, and hexamethylenetetramine have been studied. The changes in the frequencies have been examined with $Pb(OAc)_2$, $CO(NH_2)_2$, and hexamethylenetetramine when dissolved in H_2O. The last-named shows considerable changes in the C·H frequencies, suggesting hydrate formation, but shows little change in CCl_4 or Et_2O solution. The C:O frequency does not appear in the spectra of the acetates and $CO(NH_2)_2$. The possibility of the latter existing in an enol form is discussed. J. W. Smith.

Raman effect of benzene and toluene under high dispersion and resolving power. L. E. Howlett (Canad. J. Res., 1931, **5**, 572—579).—The Raman spectra of C_6H_6 and PhMe under high dispersion are compared with previous results. With both liquids a no. of new lines have been found; these arise from separation into components of previously observed lines or are entirely new. W. R. Angus.

Raman effect in aldehydes. S. S. Lu (Sci. Rep. Tsing Hua Univ., 1931, **1**, 25—32).—Data for PhCHO, heptaldehyde, and furfuraldehyde are reported and discussed. N. M. Bligh.

Raman effect in certain organic compounds. M. E. High (Physical Rev., 1931, [ii], **38**, 1837—1844).—Comparisons are made for *n*- and *iso*-forms, and the effect of shifting substituents from the *o*- to the *m*- and *p*-positions is investigated. Data are reported for Pr_2O, Pr^{β}_2O, amyl ether, propyl, butyl, amyl, and methyl propionate, *o*-, *m*-, and *p*-chlorotoluene, tolyl Me ether, chloronitrobenzene, and nitrotoluene. Some comparisons with infra-red data are made. N. M. Bligh.

Raman effect and the carbon–halogen linking. W. D. Harkins and H. E. Bowers (Physical Rev., 1931, [ii], **38**, 1845—1857).—Raman data are reported for allyl, *n*- and *iso*-propyl, *n*-, *iso*-, sec.-, and tert.-butyl, and *n*- and *iso*-amyl bromides. For halides, the effect of the length of the mol. and branching and their relation to the fundamental frequencies, force consts., and characteristic frequencies associated with the C–halogen linking are examined. N. M. Bligh.

Cathode luminescence of diamond. M. V. John (Indian J. Physics, 1931, **6**, 305—308).—The luminescence produced when three small diamonds were bombarded by cathode rays has been examined spectroscopically. One yielded a continuous spectrum extending throughout the visible region with a marked band at 4157 Å., in the same position as the fluorescence band observed by Bhagavantam in the Raman spectra (A., 1930, 1345). Another diamond showed slight absorption at this wave-length, whilst a third gave only a strong continuous spectrum. J. W. Smith.

Close connexion between extinction of fluorescence and retardation of photochemical reactions. K. Weber (Z. physikal. Chem., 1931, **B**, **15**, 18—44).—The effectiveness of anions in reducing the fluorescence of aq. Na naphthionate decreases in the order NO_3', I', Br', Cl', SO_4'' and thus diminishes as the hydration increases. $Cu^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, and $Ag^{\cdot}$ also have a considerable effect, but the alkali and alkaline-earth ions are practically indifferent. The rate at which Lauth's violet is bleached in aq.-MeOH solution in presence of diethyl-β-allylthiocarbamide as acceptor rises rapidly towards a limiting val. as the concn. of the latter is increased, and at the same time the temp. coeff. falls. Quinol, pyrogallol, and PhOH retard the bleaching and also reduce the fluorescence of Na naphthionate, the relative efficiencies being similar in each case. It is therefore concluded that the part played by these substances in both processes depends on their deactivating power on collision. At high concns. electrolytes either accelerate the bleaching somewhat or retard it only slightly, but with small concns. of some salts there is a pronounced retardation. It is therefore inferred that all electrolytes have an accelerating influence, but that with those salts which also have a retarding action this predominates at low concns. The activating effect is ascribed to the electrolyte increasing the activity of the reactants by increasing the amount of radiation absorbed, a view which is supported by observations on the effect of electrolytes on the absorption spectrum of Lauth's violet. R. Cuthill.

Fluorescence and free neutral radicals. W. A. Waters (Nature, 1931, **128**, 905—906).—Evidence supporting the view that fluorescence is associated with the re-formation of stable valency linkings from previously activated mols. is advanced.
L. S. Theobald.

Luminescence of zinc compounds. A. Kutzelnigg (Z. anorg. Chem., 1931, **201**, 323—328).—Fluorescence colours of ZnO prepared in various ways, and of some basic Zn salts, are described.
F. L. Usher.

Emission of praseodymium in alkaline-earth phosphors. I. H. Evert (Ann. Physik, 1932, [v], **12**, 107—136).—Phosphors containing sulphides and fluorides of Ca, Sr, and Ba, CaO, SrO, Al_2O_3, and sulphates of Ca and Sr, respectively, together with Pr were prepared, and the spectra of the emitted lights mapped. The results agree with the theory already developed. A. J. Mee.

Visible phosphorescence of fluorspar, excited by Schumann rays. E. Lau and O. Reichenheim (Ann. Physik, 1932, [v], **12**, 69—70).—The phosphorescence is found only at the surface of the fluorspar, corresponding with the small penetration of the rays. The emission spectrum is composed of three pairs of bands. A. J. Mee.

High efficiencies of emission from oxide-coated filaments. B. J. Thomson (Physical Rev., 1930, [ii], **36**, 1415—1417).—High efficiencies of electron emission for filaments of Ni, coated with $BaCO_3$ and $SrCO_3$, are reported. L. S. Theobald.

Thermionic emission and electrical conductivity of oxide cathodes. A. L. Reimann and L. R. G. Treloar (Phil. Mag., 1931, [vii], **12**, 1073—1088).—The thermionic current from the core metal is carried through the oxide coating mainly by Ba, Sr, or Ca ions, and re-emitted thermionically.
H. J. Emeléus.

Electrodeless conductivity measurements. W. Braunbeck (Z. Physik, 1931, **73**, 312—334).—Induced eddy currents may be used to determine the conductivity of liquid metals and alloys. Examples given are Cu and Hg at 400°. A. B. D. Cassie.

Variation of the electrical conductivity of molten bismuth with content of bismuth chloride. W. Braunbeck (Z. Physik, 1931, **73**, 335—347).—The influence of dissolved Cl on the electrical conductivity of Bi is small; $7\frac{1}{2}$ at.-% of Cl did not reduce the conductivity to $\frac{1}{2}$ its original value.
A. B. D. Cassie.

Conductivity of compressed metallic powders. C. Kantorowicz (Ann. Physik, 1931, [v], **12**, 1—51).—The resistance of metal powders of different particle size was found under pressures up to 4200 atm. The resistance is different from that of the compact metal. The powder changes under pressure, probably solidifying, and this accounts for a relatively complex relationship between the resistance and the conditions of the experiment. The resistance is not const., but varies with time. For increasing pressure the resistance is given by $1/R=c\sqrt{P}+C$, where c and C are consts. depending on the previous treatment of the powder. For the same previous treatment, the pressure–resistance curves are reproducible. They are irreversible. Ohm's law is not satisfied. The temp. coeff. of resistance is negative for $P=0$, but for higher pressures is negative for rising temp. and positive for falling temp. Coherer action is sometimes shown at high pressures.
A. J. Mee.

Dielectric constant of commercial nitrogen at high pressures. J. W. Broxon (Physical Rev., 1931, [ii], 38, 2049—2050; cf. this vol., 3).—The variation of $(K-1)$ with the pressure, for N_2 (99% pure), up to 167 atm., was investigated. N. M. Bligh.

Dipole moments of molecules with mutually independent (ideally decoupled) dipole groups. L. Ebert and K. Hojendahl (Z. physikal. Chem., 1931, **B**, **15**, 74—78).—It is deduced theoretically and verified from experimental data that the total dipole moment of a mol. which has two similar independent polar groups each of moment μ, say at the ends of a very long aliphatic chain, is $\sqrt{2}\mu$. R. Cuthill.

Change in dielectric constant of thin layers of ZnS–Cu phosphors on illumination with different wave-lengths of light. E. Breunig (Ann. Physik, 1931, [v], **11**, 863—884).—The spectral distribution of increase in dielectric const. of layers $56—80\times10^{-4}$ cm. thick of ZnS–Cu phosphors follows closely the distribution of wave-lengths exciting phosphorescence. A. B. D. Cassie.

Electric moment and molecular structure. VI. Variation of electric moment with temperature. C. P. Smyth, R. W. Dornte, and E. B. Wilson (J. Amer. Chem. Soc., 1931, **53**, 4242—4260; cf. A., 1931, 1112).—The calculation of the energy of a system of dipoles rotating about a common axis, either in terms of the classical or the wave mechanics, leads to the conclusion that the moment may vary with temp. The electric moments of $CH_2Cl{\cdot}CH_2Cl$ and $CH_2Cl{\cdot}CH_2Br$ vary markedly with temp., whilst that of EtOAc shows no significant variation, probably because of the high mutual potential energy of the dipoles. The moment of Et succinate increases from 0° to 180°, probably because increasing vibrational energy enables more and more mols. to open out to an extended structure, the moment at 180° being identical with those of the very long-chain dicarboxylic acid esters. The moment of a mol. containing two or more dipoles, the axes of which may alter their positions relative to one another, may be affected by both temp. and environment (solvent).
H. F. Johnstone (*c*).

Dielectric constants and molecular polarisations of binary liquid mixtures. W. Graffunder and E. Heymann (Z. Physik, 1931, **72**, 744—762).—Using an improved resonance method the dielectric consts. of a series of binary liquid mixtures have been measured and the corresponding mol. polarisations calc. Mixtures of two polar liquids show no anomalies other than those shown where only one of the liquids is polar. The results are discussed with reference to so-called association.
J. W. Smith.

Physics of the nitrobenzene "Kerr" cell. III. Distribution of a strong electrical alternating field in the nitrobenzene Kerr cell. IV. Accuracy of Kerr's law for nitrobenzene in strong alternating electric fields. F. Hehlgans (Physikal. Z., 1931, **32**, 951—957, 971—974; cf. A., 1931, 1220).—III. Experiments with alternating fields show that the field distribution in the $PhNO_2$ Kerr cell is always homogeneous. With impure $PhNO_2$, however, the field distribution was not homogeneous.

IV. For pure $PhNO_2$ in strong alternating electric fields Kerr's law holds. A. J. Mee.

Theory of Kerr effect in wave mechanics. T. Neugebauer (Z. Physik, 1931, **73**, 386—411).

Refraction and dispersion of gaseous hydrocarbons. S. Friberg (Z. Physik, 1931, **73**, 216—222).—Refraction and dispersion of wave-lengths between 5800 and 2300 Å. were measured for C_3H_6 and C_3H_8, and the results are fitted to Cauchy dispersion formulæ: dispersion of these gases is very susceptible to impurities. A. B. D. Cassie.

Refractive index of fused sodium nitrate. E. van Aubel (Bull. Acad. roy. Belg., 1931, [v], **17**, 1158—1160).—Assuming a mean val. of 11·54 for the mol. refraction of liquid $NaNO_3$ to hold up to the crit. temp. and using the val. 0·625 calc. from viscosity data for the crit. density, the refractive index of $NaNO_3$ at its crit. point is 1·127, in good agreement with the vals. found for other substances at the crit. point (A., 1912, ii, 1013). J. W. Smith.

Nature of valency linkings and circular dichroism. J. P. Mathieu (Compt. rend., 1931, **193**, 1079—1081).—A solution of acid Cr^{III} tartrate prepared by dissolving not more than 1/3 g.-atom of Cr [as $Cr(OH)_3$] in 1 mol. of tartaric acid, when first prepared, is bluish-violet, contains the Cr as a coloured Cr^{III} cation, and exhibits normal rotatory dispersion, with no circular dichroism. On keeping, the colour slowly changes to deep violet, the Cr passing into a coloured complex anion no longer precipitable by NH_3, the dispersion increases and becomes anomalous, and circular dichroism appears, probably proportionally to the amount of the complex anion formed. In the first case the chromophore is united by a heteropolar, in the second by a homopolar, valency (cf. A., 1925, ii, 1119). C. A. Silberrad.

Rotatory magnetic polarisation of liquids and liquid mixtures. J. Verhaeghe (Bull. Acad. roy. Belg., 1931, [v], **17**, 1221—1234).—The rotatory magnetic power of quinoline and of mixtures of quinoline with C_6H_6 and CCl_4 has been measured. The results are discussed. J. W. Smith.

Optically active properties of inorganic compounds. W. Kuhn and A. Szabo (Z. physikal. Chem., 1931, **B**, **15**, 59—73).—In aq. solution K Cr tartrate has a strong absorption band at 3700 and a weak band at 5960 Å., but the circular dichroism and anomalous rotation are confined to the latter. The anisotropy factor is not, however, const. over the whole band, which indicates that in respect of the electron transitions giving rise to it the band is far from being homogeneous. The connexion between the dichroism and the rotation may be expressed satisfactorily by the equation deduced previously (A., 1930, 980). A survey of the available data shows that in their optically active properties inorg. compounds closely resemble org. compounds. The rotation of an inorg. compound is normally contributed in the main by a comparatively weak absorption band which represents only a small fraction of the total absorptive power of the compound. An instance of optical superposition among Co compounds is reported. R. Cuthill.

Theory of homopolar valency in polyatomic mols. M. Born (Angew. Chem., 1932, **45**, 6—8).—A theoretical discussion in terms of electron spins. E. S. Hedges.

Valency variation and at. structure. M. Gomberg (Science, 1931, **74**, 553—557).—An address. L. S. Theobald.

State of molten salts. P. Walden (Z. physikal. Chem., 1931, **157**, 389—421).—It is found empirically that for the molten tetra-alkylammonium picrates at 140° λc=const., where λ is the equiv. conductivity and c the temp. coeff. of the conductivity. A similar relation is valid for the molten alkali chlorides, bromides, and iodides at 800°, and the val. of $\lambda\sqrt{M}$ at the m. p., where M is the mol. wt., is also const. for these compounds. At the m. p., $\lambda\eta\sqrt{M}$, where η is the viscosity, has the val. 10·5 for molten KNO_3, $NaNO_3$, NaCl, KCl, and NaOH, and the picrates in aq. and non-aq. solution at infinite dilution give the same figure. It is therefore deduced that the molten salts are completely dissociated. Utilising the relations $l_{pi}\eta$=const. for the conductivity l_{pi} of the picrate ion, and $l_{\text{cat.}}\eta\sqrt{M_{\text{cat.}}}$=const. for the conductivities, $l_{\text{cat.}}$, of the tetra-alkylammonium ions, it has been possible to calculate the equiv. conductivities at the m. p. of the picrates, and a similar calculation has been made for alkali salts. The results indicate that the molten salts are practically completely ionised. With the picrates of the mono-, di-, and tri-alkylammonium bases, however, the degree of dissociation at the m. p. varies from 0·65 to 0·095. R. Cuthill.

Calculation of molecular lattice dimensions from resonance forces. E. Cremer and M. Polanyi (Z. physikal. Chem., 1931, **B**, **14**, 435—442).—Assuming that the energy of a mol. lattice is equal to the difference between an attraction potential, which varies with the intermol. distance in accordance with London's theory (A., 1931, 149), and a repulsion potential, which is due to quantum mechanical resonance and can be calc. from optical data, it has been possible to calculate the intermol. distance in the lattices of H_2, HCl, HBr, and HI. R. Cuthill.

Relation between b. p. and chemical constitution. II. K. Billig (Svensk Kem. Tidskr., 1931, **43**, 281—293).—The manner in which the association factor Kf (cf. this vol., 13) diminishes as the degree of association rises is illustrated by reference to $(H_2O)_x$, and the relevant vals. of Kf are employed to calculate the percentage of associated mols. in the fatty acids. It is shown that with these compounds association takes place through principal valencies. For derivatives of the fatty acids conditions are more complicated; with open-chain esters and acid anhydrides the auxiliary valencies are the principal means of association, whereas with ring compounds such as lactones the principal valency type of association preponderates. The latter type is found also for H_2O, and it is shown that the 4 valency linkings of O must be directed towards the corners of a tetrahedron, as in the case of the C atom; the mol. of $(H_2O)_6$ thus resembles that of C_6H_6. Various other types of 6-membered ring are discussed, including those of NH_3, N_2H_4, and the heterocyclic ring formed by N_2H_4,H_2O, and those of the O compounds of N and the org. NO_2-compounds. This type of ring formation is very general, although in the case of inorg. compounds the rings are not stable and break down when the substance vaporises. H. F. Gillbe.

An aspect of co-ordination. J. Kenner (Nature, 1931, **128**, 1000—1001).—Theoretical. L. S. Theobald.

Specific heat of ferromagnetics and Ewing's model of the magnetic atom. J. R. Ashworth (Nature, 1931, **128**, 1003).—A discussion. L. S. Theobald.

Ferromagnetic moment and the periodic system. C. Sadron (Compt. rend., 1931, **193**, 1070—1073; cf. A., 1931, 791).—The magnetic moments (in Weiss magnetons) of the following elements in solid solution in Ni or Co are: Cu 2·09, Au 2·3, Si 17·8, Sn 18·0, V 23·9, Sb 24·4. They support the conclusion, previously arrived at, that elements in the same column of the periodic table have the same moment. Ru is an exception, the moment being 11, that of pure Fe, and not that of Fe in Ni (14). Assuming the foregoing to hold, the moments of elements in the line of Fe plotted against at. no. show an ascending (Cu—V) and a descending (V—Ni) branch with intervals of approx. 5 and 4 magnetons, respectively, save between Si and Ti. C. A. Silberrad.

Magnetic behaviour of cobalt atoms. H. Vatter (Z. Physik, 1931, **73**, 260—272).—A method for obtaining at. rays of metals of high m.p. is described. The greatest moment of Co is 5·8 Bohr magnetons. A. B. D. Cassie.

Magnetic moment of quadrivalent cobalt. (Mlle.) A. Serres (Compt. rend., 1931, **193**, 1327—1328).—The magnetic susceptibility of $MgCoO_3$ (cf. A., 1896, ii, 647) has been determined from −182·7° to 549·4°. $1/\chi$ is related linearly to temp. above 233°, the Curie point is −164·5° abs., the Curie const. 4·261, and the magnetic moment of Co^{IV} 29 experimental magnetons. C. A. Silberrad.

Magnetic properties of iron above the Curie point. L. Néel (Compt. rend., 1931, **193**, 1325—1326).—By determining the ferromagnetic (θ_f) and paramagnetic (θ_p) Curie points and the Curie const. (c) for a series of Fe–Sn (87·21—92·23% Fe) and Fe–Si (89·72—97·04% Fe) alloys and extrapolating the vals. for β-Fe (which when unalloyed changes to γ-Fe before the required temp. is attained) are deduced as θ_f 772°, θ_p 815°, c 0·02256. C. A. Silberrad.

Paramagnetic susceptibility of chromic chloride and its hexahydrates. J. W. Shih (Sci. Rep. Tsing Hua Univ., 1931, **1**, 83—91).—Using $Mn_2P_2O_7$ as the standard substance for comparison the vals. $\times 10^6$ obtained per g. were: for the anhyd. salt 44·5, for $[CrCl_2(H_2O)_4]Cl,2H_2O$ 24·0, and for $[Cr(H_2O)_6]Cl_3$ 12·6. N. M. Bligh.

Theory of magnetisation curves of isotropic ferromagnetics in medium and strong fields. R. Gans (Physikal. Z., 1932, **33**, 15—17).

Variations of atomic moment in paramagnetic substances. Magnetic states and different varieties of the same ion. G. Foëx (J. Phys. Radium, 1931, [vii], **2**, 353—375).—The bent graphs obtained by plotting the inverse of the coeff. of magnetisation against the temp., and the different magnetic moments shown by different samples of the same substance within the same temp. range, are discussed on the basis of the data for many paramagnetic substances. N. H. Hartshorne.

Diamagnetism of free electrons in metals. P. Y. Chou (Sci. Rep. Tsing Hua Univ., 1931, **1**, 1—7).—Mathematical. N. M. Bligh.

Magnetic properties of gold–iron alloys. J. W. Shih (Physical Rev., 1931, [ii], **38**, 2051—2055).—The change in susceptibility with temp. and composition was investigated for alloys containing 0·07—10 wt.-% Fe. Alloys containing 0·1—5% Fe are paramagnetic. N. M. Bligh.

Classification of paramagnetic atoms, molecules, and ions according to field and temperature. E. C. Wiersma (Wis- en Natuurkund. Tijdschr., 1930, **5**; Chem. Zentr., 1931, i, 2442—2443).—Three groups, viz., (i) weakly paramagnetic metals such as Na, K, Pt, and Pd with susceptibility practically independent of temp., (ii) paramagnetic gases, O_2 and NO, and (iii) salts such as $NiSO_4$, $CrCl_3$, $FeCl_2$, and those of Co, are distinguished. The extent to which the Curie–Weiss law holds for each group is discussed. L. S. Theobald.

Diamagnetism of liquid mixtures. J. Farquharson (Nature, 1932, **129**, 25).—The susceptibility–concn. curve for $CHCl_3$–$COMe_2$ mixtures shows a max. at equimol. proportions and two minima, but the departure from additivity is 3—4%. The two ends of the curve show a slight rise in diamagnetism. The susceptibilities found are $-0{\cdot}60\times10^{-6}$ for $COMe_2$, and $-0{\cdot}498\times10^{-6}$ for $CHCl_3$. L. S. Theobald.

Parachor measurements applied to the study of the constitution of polysulphides, polyselenides, and mixed chains of sulphur and selenium. A. Baroni (Atti R. Accad. Lincei, 1931, [vi], **14**, 28—32; cf. A., 1929, 1270).—Parachor measurements have been made of various Et_2 sulphides, selenides, and sulphoselenides. These indicate that compounds containing 3 atoms of S or Se have a straight chain. This becomes branched in the tetrasulphide and converted into a ring of 3 S atoms in the two isomeric pentasulphides. O. J. Walker.

Capillarity. XVI. Capillary rise of liquids between parallel plates. K. Schultze (Kolloid-Z., 1931, **57**, 277—285).—The capillary rise of H_2O between parallel glass plates is independent of the width of the plates (in accordance with the usual formula) when this exceeds 2 mm.; when the width of the plates is between 2·0 and 0·4 mm. the capillary

rise decreases as the width of the plates is reduced, and the distance apart is kept const. When the plates are of unequal width, that of the narrower plate determines the rise, but the rise is greatest when two identical plates are used. The effect of increasing the width of the plates increases as the distance between the plates is decreased.
E. S. HEDGES.

Densities and partial molal volumes of ammonia for the ammines of calcium and barium chlorides. L. J. GILLESPIE and H. T. GERRY (J. Amer. Chem. Soc., 1931, **53**, 3962—3968; cf. A., 1921, ii, 116; 1927, 92).—Determinations of d^{25} have been made with the aid of new methods which do not necessitate the isolation of the pure ammine and are suitable for use with compounds having such high decomp. pressures that the ordinary methods are inapplicable. W. C. FERNELIUS (*c*).

Aitken condensation nuclei. A. R. HOGG (Nature, 1931, **128**, 908). L. S. THEOBALD.

Two forms of molecular hydrogen. A. CAMPETTI (Nuovo Cim., 1931, 8, xvii—xxvii; Chem. Zentr., 1931, ii, 190).—A *résumé*. A. A. ELDRIDGE.

Diffuse scattering of *X*-rays from sylvine at low temperature. G. E. M. JAUNCEY and G. G. HARVEY (Physical Rev., 1931, [ii], 38, 1925—1931).—Intensities of wave-length 0·43 Å. scattered in the angle range 25—90° at 90° and 300° abs. are compared, and the relation thereto of temp. effect and the at. structure factor is investigated. N. M. BLIGH.

Intensity of total scattering of *X*-rays by monatomic gases. Y. H. WOO (Sci. Rep. Tsing Hua Univ., 1931, **1**, 55—67; cf. A., 1930, 1334; 1931, 665).—Theoretical. N. M. BLIGH.

Absorption of soft *X*-rays in gases. R. G. SPENCER (Physical Rev., 1931, [ii], 38, 1932—1937).—Absorption coeffs. of air, A, and O_2 in the range 1·5—7 Å. and in the immediate neighbourhood of the *K* absorption limit are in agreement with the absorption law. N. M. BLIGH.

Use of ionisation determination methods with *X*-rays. W. STOCKMEYER (Ann. Physik, 1932, [v], **12**, 71—106).—Ionisation is proportional to absorbed energy. The proportionality factors for EtBr and SO_2 are determined, these being frequently used in ionisation chambers because they absorb *X*-rays more strongly than air. For EtBr the absorption is determined for different wave-lengths, as there is a distinct change in the factor for wave-lengths shorter than the *K*-limit of Br. A. J. MEE.

Dispersion of *X*-rays in calcite. L. A. PARDUE (Physical Rev., 1931, [ii], 38, 1808—1815).—The $K\alpha_1$ line from a Mo target was used; $(1-\delta)$ was $(2{\cdot}001\pm0{\cdot}009)\times10^{-6}$. The intensities of radiation reflected from calcite mirrors in the neighbourhood of the crit. angle were in fair agreement with theory. N. M. BLIGH.

Growth of crystals. F. STÖBER (Chem. Erde, 1931, 6, 453—467).—A discussion of certain anomalies in the growth of crystals for which explanations are offered (cf. A., 1931, 1028, 1030). L. J. SPENCER.

Crystallisation of lead nitrate. Effect of foreign substances in the mother-liquor. P. GAUBERT (Bull. Soc. franç. Min., 1930, **53**, 157—171; Chem. Zentr., 1931, i, 2433).—Crystals of $Pb(NO_3)_2$ grow more quickly in the presence of methylene-blue, but without a change of form. The coloured crystals show clear striations on the cubic faces, whilst a cubic–octahedral combination from pure solution shows in the coloured solution a quicker growth at the octahedral faces. $Sr(NO_3)_2$ crystals are coated with $Pb(NO_3)_2$ from a coloured solution of the latter and show its characteristics. $Ba(NO_3)_2$ grows in $Pb(NO_3)_2$ solution, but is coloured with difficulty. When methylene-blue is suspended in the solution the $Pb(NO_3)_2$ crystallises in platelets especially at higher temp., but at lower temp., cubes can appear. With rosolic acid, elongated octahedra formed on certain cubic faces make the crystals appear to be orthorhombic. L. S. THEOBALD.

Change of the distance between adjacent atoms in certain elements and alloys which results when the cubic face-centred lattice changes to the cubic body-centred or hexagonal lattice. H. PERLITZ (Acta Comm. Univ. Tartuensis, 1931, 72 pp.).—Calculations have been made from published data on various metals, binary and ternary alloys, and steels. The calc. change is in general due exclusively to change of the co-ordination no. and type. It ranges from −1·3% to −3·3% (mean 2·25%) for transition from the face-centred to the body-centred cubic lattice, and from −1·1% to +5·1% for transition from the densest cubic to the densest hexagonal lattice; for the second case it tends to zero as the axial ratio of the hexagonal lattice approaches 1·633.
H. F. GILLBE.

A two-dimensional space lattice? R. C. MENZIES (Nature, 1931, **128**, 907).—When 10% KI solution is added to a saturated, aq. solution of dimethylthallium iodide or when a warm aq. solution is cooled, part of the Tl compound separates on the surface in a regular pattern; each crystal is equidistant from 6 others. The effect is transient. L. S. THEOBALD.

A two-dimensional space lattice? W. BAKER (Nature, 1931, **128**, 1078).—An explanation of the unusual crystallisation (cf. preceding abstract) is advanced, and similar cases are recorded.
L. S. THEOBALD.

Specific surface properties of molecular fields. Structure of active charcoals and the inversion of surface effects and heats of activation. II. B. V. ILJIN and J. P. SIMANOV (J. Gen. Chem. Russ., 1931, **1**, 567—568).—The presence of 1% of graphite added to active C can be detected by *X*-ray spectrum methods; this amount of graphite suffices to cover only 20% of the total surface with a unimol. layer, showing that the inversion of Traube's series exhibited by certain charcoals not giving the graphite lines cannot be due to graphitisation of their surface.
R. TRUSZKOWSKI.

Structure of ferromagnetic ferric oxide. J. THEWLIS (Phil. Mag., 1931, [vii], **12**, 1089—1106).—Ferromagnetic Fe_2O_3 is cubic; unit cube 8·4 Å.; 12 mols. Fe_2O_3 in unit cube; space-group O^6 (or O^7) or T^4. The structure is very similar to that of Fe_3O_4 (cubic; unit cube 8·4 Å.; 8 mols. Fe_3O_4 in unit cell). Fe and O atoms occupy the same positions as in

Fe_3O_4. The possible arrangements of the extra 4 O atoms are discussed. H. J. Emeléus.

Magnetic properties and crystalline structure of different varieties of anhydrous cobalt sulphate. R. Hocart and (Mlle.) A. Serres (Compt. rend., 1931, **193**, 1180—1182).—*X*-Ray examination of Chatillon's two varieties of $CoSO_4$, of magnetic moment 25 and 26 magnetons (cf. A., 1928, 454), and of the variety obtained by Klobb (cf. A., 1892, 941), also of moment 26 magnetons, shows that the structures of the two latter are identical—orthorhombic, *a* 4·6$_5$, *b* 6·7$_1$, *c* 8·4$_5$ Å., 4 mols. in unit cell—whilst that of the first is identical as regards shape and dimensions of the unit cell, but differs in the arrangement of the atoms therein. C. A. Silberrad.

Structure of compounds of sulphur with iodides. I. Compounds of sulphur with tri-iodides. E. Hertel (Z. physikal. Chem., 1931, **B, 15**, 51—57).—Both $CHI_3,3S_8$ and $AsI_3,3S_8$ crystallise in the trigonal system with the probable space-group C^1_{3v}, and the dimensions of the unit cell, which in each case contains 1 mol., are *a* 14·1, *b*, 24·4, *c* 4·44, and *a* 14·2, *b* 24·6, *c* 4·48 Å., respectively. The S_8 mols. in these compounds are probably three-dimensional systems, with the min. symmetry C_s. The f.-p. diagrams show that AsI_3 and CHI_3 are not miscible in the solid state, whereas $AsI_3,3S_8$ and $CHI_3,3S_8$ are miscible in all proportions.
R. Cuthill.

Crystal structure of potassium tantalum and potassium niobium heptafluorides and of potassium titanium hexafluoride. F. Zambonini (Bull. Soc. franç. Min., 1930, **53**, 443—468; Chem. Zentr., 1931, i, 2451).—K_2TaF_7 is monoclinic with $a : b : c =$ 0·6718 : 1 : 0·9198, β 90° 15′, and *d* 4·056; K_2NbF_7, monoclinic, has $a : b : c = 0{\cdot}6711 : 1 : 0{\cdot}9209$, β 89° 48′, and *d* 3·21. Anhyd. K_2TiF_6, trigonal, d^{15} 3·012, shows weak double refraction; it is isomorphous with $(NH_4)_2TiF_6$ and $(NH_4)_2SnF_6$. L. S. Theobald.

Bismuth thiocarbamide compounds. C. Gottfried and H. Steinmetz (Veröff. Kaiser Wilhelm-Inst. Silikatforsch., 1929, **2**; Chem. Zentr., 1931, i, 2435).—The *compound*, $BiCl_3,3CS(NH_2)_2$, has *a* 13·29, *c* 7·02, *r* 14·81 Å.; 1 mol. per unit rhombohedron; space-group C^4_3; $BiCo(CN)_6,6CS(NH_2)_2$ has *a* 13·92, *c* 12·48, *r* 9·13 Å.; 1 mol. per unit rhombohedron; space-group probably D^5_{3d}. $[Bi{\cdot}6CS(NH_2)_2][X(CN)_6]$, where X is Cr and Fe, have been obtained. Microcryst. ppts. are formed in Bi salt–$CS(NH_2)_2$ solutions with $K_3Co(NO_2)_6$, $K_3Co(C_2O_4)_3$, and $K_3Cr(CNS)_6$; the oxalate compound contains 6 mols. of $CS(NH_2)_2$ to 1 atom. of Bi. L. S. Theobald.

Crystal lattice of calcium metaborate. W. H. Zachariasen (Proc. Nat. Acad. Sci., 1931, **17**, 617—619).—CaB_2O_4 is orthorhombic with 4 mols. per unit cell; *a* 6·19, *b* 11·60, *c* 4·28 Å., space-group *Pnca* (V^{14}_h). N. H. Hartshorne.

Spinels. IV. Manganese and cadmium sulphochromites. L. Passerini and M. Baccaredda (Atti R. Accad. Lincei, 1931, [vi], **14**, 33—37; cf. A., 1931, 289).—These two compounds crystallise in the cubic system with a lattice of the spinel type. $MnCr_2S_4$, *a* 10·045±0·005 Å., *v* 1013·56×10^{-24} c.c., $d_{calc.}$ 3·736, $d_{obs.}$ 3·44; $CdCr_2S_4$, *a* 10·190±0·005 *v* 1058·09×10^{-24} c.c., $d_{calc.}$ 4·295. O. J. Walker.

Sulpho-salts with spinel structure. G. Natta and L. Passerini (Atti R. Accad. Lincei, 1931, [vi], **14**, 38—43; cf. preceding abstract).—The spinel type structure of linnæite is confirmed; *a* 9·41±0·01 Å. (cf. A., 1927, 502). $ZnCr_2S_4$ also belongs to the spinel type; *a* 9·92±0·02, *v* 976·10×10^{-24} c.c., $d_{calc.}$ 4·05.
O. J. Walker.

Lattice dimensions of spinels. G. L. Clark, A. Ally, and A. E. Badger (Amer. J. Sci., 1931, [v], **22**, 539—546).—Results are tabulated. C. W. Gibby.

Relationship between structures of argentite and acantite. J. Garrido (Anal. Fís. Quím., 1931, **29**, 505—513).—Published data indicate that acantite possesses a pseudocubic structure, whilst argentite has a multiple lattice of dimensions similar to those of the acantite lattice; the structure of synthetic Ag_2S is similar. The structural relationships and stability conditions are discussed. H. F. Gillbe.

Crystal structure of argentite and acantite. J. Palacios and R. Silva (Anal. Fís. Quím., 1931, **29**, 514—515).—A criticism of Garrido's conclusions (cf. preceding abstract). H. F. Gillbe.

Structure of the phenacite–dioptase group. Phenacite, Be_2SiO_4. C. Gottfried (Jahrb. Min. Beil.-Bd., 1927, **A**, **55**, 393—400; Chem. Zentr., 1931, i, 2452).—Rotation diagrams about [001] and [211] give for Be_2SiO_4 *a* 12·49, *c* 8·26 Å., 18 mols. in the hexagonal unit cell; space-group C^2_{3i}. Willemite, *a* 14·14, *c* 9·58 Å., troostite, *a* 14·21, *c* 9·62 Å., and dioptase, *a* 14·66, *c* 7·83 Å., have the same space-group and no. of mols. per unit cell.
L. S. Theobald.

Crystal structure of marcasite. M. J. Buerger (Amer. Min., 1931, **16**, 361—395).—The unit cell has *a* 3·37, *b* 4·44, *c* 5·39 Å.; space-group V^{12}_h. Marcasite appears to be composed of Fe and S in the at. state with almost identical radii (1·12 Å.).
Chemical Abstracts.

Crystal structure of rubidium azide. W. Büssem, P. Rosbaud, and P. Günther (Z. physikal. Chem., 1931, **B**, **15**, 58).—The structure advocated by Pauling (A., 1930, 983) is accepted. R. Cuthill.

Structure of the azides. E. Bergmann and W. Schütz (Nature, 1931, **128**, 1077—1078).—Sutton's conclusions (A., 1931, 1359) are criticised; an open-chain structure for the azides is preferred. The dipole moments of Ph, *p*-chlorophenyl, and *p*-bromophenyl azides are 1·55, 0·47, and 0·64×10^{-18} e.s.u., respectively. L. S. Theobald.

Crystal structure of an organic molecular compound of the type AB_2. E. Hertel and K. Schneider (Z. physikal. Chem., 1931, **B**, **15**, 79—83).—The crystals of the compound of stilbene with 2 mols. of *s*-trinitrobenzene belong to the triclinic system and the unit cell has *a* 12·7, *b* 15·4, *c* 7·7 Å., and contains 2 mols. R. Cuthill.

Hysteresis effects in magnetostriction. A. Schulze (Ann. Physik, 1931, [v], **11**, 937—948).

Hall effect and superconductivity. I. Kikoin and B. Lasarev (Nature, 1932, **129**, 57—58).—

Superconductors show a relatively small val. of the Hall coeff. L. S. THEOBALD.

New method of investigating the modes of vibration of quartz crystals. J. A. STRONG (Nature, 1932, **129**, 59). L. S. THEOBALD.

Allotropic modification of solid barium. E. RINCK (Compt. rend., 1931, **193**, 1328—1330).—Pure Ba is acted on by CO_2, and must be distilled in A. The twice-distilled metal has m. p. 710 ± 2°, $d_4^{17·5}$ 3·74. The cooling and resistance–temp. curves show discontinuities at 375°, the α variety being stable below, the β above, that temp. (cf. A., 1931, 416). C. A. SILBERRAD.

Allotropism of phosphorus. V. N. IPATIEV, A. A. VVEDENSKI, and A. V. FROST (J. Gen. Chem. Russ., 1931, **1**, 632—640).—The sp. heat and inflammation point of red P increase with rise of temp. at which it was prepared, from 2·17 and 330° at 315° to 2·34 and 450° at 589°. The sp. heat of red P is unaffected by varying the pressure at which it was prepared from 1 to 220 atm. Red P is probably violet P adsorbed on white P. R. TRUSZKOWSKI.

Superconductivity at high frequencies. J. C. MCLENNAN, A. C. BURTON, A. PITT, and J. O. WILHELM (Nature, 1931, **128**, 1004).—Pb and Sn become superconducting with currents of frequencies of the order 10^7 per sec. The transition temp. are lowered as frequency is increased. L. S. THEOBALD.

Thermodynamic properties of dichlorodifluoromethane, a new refrigerant. IV. Specific heat of liquid and vapour and latent heat of vaporisation. R. M. BUFFINGTON and J. FLEISCHER. **V. Correlation, checks, and derived quantities.** R. M. BUFFINGTON and W. K. GILKEY (Ind. Eng. Chem., 1930, **23**, 1290—1292, 1292—1294; cf. A., 1931, 675).—IV. Measurements of the sp. heat of CCl_2F_2 at atm. pressure in a flow calorimeter at 0°, 25·8°, and 49·9° indicate that it follows the equation $C_p=17·0+0·0279t$ g.-cal. per mol. The heat capacity of the liquid measured by the method of mixtures at 17° is 30·3 g.-cal. per mol., and by using an electric heating method is 25·4 at —43°. The latent heat of vaporisation as determined by an electrical heating method is 4880 g.-cal. per mol. at —29·8° (the b. p.), 4100 at 23°, and 3960 at 28°. Using Kundt's method the ratio C_p/C_v for the vapour at 25° and atm. pressure is found to be 1·139.

V. Data previously recorded are summarised and cross-checked with one another. J. W. SMITH.

Explosion method for the determination of specific heats of gases at high temperatures. B. LEWIS (J. Amer. Chem. Soc., 1931, **53**, 4227—4228).—Sp. heat determinations were made with mixtures of H_2 and O_2, the velocity of the detonation wave being made the same in all mixtures by addition of suitable amounts of A or He, or mixtures of the two. The effect on the sp. heats of variations in the type, size, and material of the diaphragm pressure indicator and the explosion chamber is also investigated. C. J. WEST (*c*).

Nature of liquids. L. G. CARPENTER (Nature, 1932, **129**, 60).—It is shown that the sp. heats of the elements near the m. p. support the previously expressed view (A., 1931, 1360; this vol., 14) that liquids, especially near the m. p., resemble solids more nearly than gases. L. S. THEOBALD.

Determination of the internal latent heats of vaporisation of liquids. N. DE KOLOSOVSKI and I. S. MESHENIN (Bull. Soc. chim., 1931, [iv], **49**, 1461—1465, and J. Gen. Chem. Russ., 1931, **1**, 616—619).—A known wt. of liquid is allowed to evaporate from a continuously-evacuated vessel contained in an adiabatic calorimeter. From the internal latent heat thus determined the total latent heat is calc. for various temp. for $Bu^{\beta}OH$, $CHCl_3$, CCl_4, C_6H_6, PhMe, PhEt, and C_5H_5N. C. W. DAVIES.

M. p. of butyl ether. R. C. ARCHIBALD (J. Amer. Chem. Soc., 1931, **53**, 4452).—The m. p. is 177·8±0·2° abs. C. J. WEST (*c*).

Rational unit in thermal conduction. P. VERNOTTE (J. Phys. Radium, 1931, [vii], **2**, 376—380).—A discussion. The name "fourier" for the unit of thermal conduction is preferred, the heat being measured in joules. N. H. HARTSHORNE.

Thermal conductivity of inert gases. M. CURIE and A. LEPAPE (J. Phys. Radium, 1931, [ii], **2**, 392—397).—A more detailed account of work already noted (this vol., 13).

Thermal conductivities of certain approximately pure metals and alloys at high temperatures. L. C. BAILEY (Proc. Roy. Soc., 1931, **A**, **134**, 57—76).—The thermal conductivities of a number of metals and alloys have been determined by the guard-tube method. The conductivity of Al reaches a max. at about 225° and then decreases to 550°; Ag reaches a min. at about 400° and then increases to 575°. The val. for Zn decreases gradually and continuously from —170° to 370°, whilst Cd shows an abrupt fall and rise near 50°, after which the normal steady decrease occurs. The conductivity of brass increases linearly with rise of temp. up to 125°, after which it tends to become const. at 0·335 up to 450°. With platinoid, the val. increases linearly with rise of temp. Support is obtained for the view that the conductivity of a metal increases as the degree of purity is increased. L. L. BIRCUMSHAW.

Thermal conductivities of the saturated hydrocarbons in the gaseous state. W. B. MANN and B. G. DICKINS (Proc. Roy. Soc., 1931, **A**, **134**, 77—96).—The thermal conductivities and temp. coeffs. of CH_4, C_2H_6, C_3H_8, C_4H_{10}, n-C_5H_{12}, and n-C_6H_{14} have been determined by the hot-wire method. A hyperbolic curve is obtained by plotting the thermal conductivity at 0° against the mol. wt., the relation between the two being given by $(K_0-0·00002227)\times(M-5·53)=0·0005241$. Plotting the temp. coeff. against the mol. wt. gives a curve which passes through a max. L. L. BIRCUMSHAW.

Density and deviation from Avogadro's law of nitrous oxide. At. wt. of nitrogen. T. BATUECAS (Anal. Fis. Quím., 1931, **29**, 538—551, and J. Chim. phys., 1931, **28**, 572—586).—

N_2O, prepared by 10 different methods, had *d* 1·9804±0·0001 g. per litre. At 0·667 and 0·333 atm. pressure the densities were 1·9746 and 1·9694, respectively; the factor $1+\lambda$ is therefore 1·0085, a val. which differs by more than 0·1% from previous determinations. The compressibility of N_2O is 112×10^{-6} and the calc. at. wt. of N is 14·007. (Cf. A., 1931, 1222.) H. F. Gillbe.

Vapour pressure, surface tension, and density of osmium tetroxide. E. Ogawa (Bull. Chem. Soc. Japan, 1931, 6, 302—317).—The v. p. of OsO_4 over the range 15—130° has been redetermined by means of a glass spring manometer. From these data, the m. p. (40·6—40·7°), b. p. (131·2°), heats of sublimation (11,640 g.-cal.), vaporisation, and fusion (1540 g.-cal.), Trouton's const. (21·5), parachor (157·7), and crit. temp. (405°) are calc. OsO_4 is a normal liquid above 75°, slight association occurring at lower temp. Krauss' statement (A., 1925, ii, 894) that solid OsO_4 exists in two forms was not confirmed. D. R. Duncan.

Determination of the coefficient of cubical expansion of solid benzoic acid by means of a gas-filled dilatometer. E. R. Smith (Bur. Stand. J. Res., 1931, 7, 903—905).—The coeff. of cubical expansion of BzOH between 15° and 30°, determined by the method described, is 0·00052 per degree. E. S. Hedges.

Isotherms of hydrogen, carbon monoxide, and their mixtures. D. T. A. Townend and L. A. Bhatt (Proc. Roy. Soc., 1931, **A**, **134**, 502—512; cf. A., 1929, 1227).—The isotherms of H_2, CO, and mixtures of the two in the mol. proportion 2 : 1, 1 : 1, and 1 : 2 have been determined at 0° and 25° over a pressure range extended up to 600 atm. Each isotherm is expressed in the form $pv_A=a+bp+cp^2+dp^3$, the vals. of the consts. being tabulated. The observed deviations from the "additive vol." and "additive pressure" laws are discussed. Between pressures of about 300 and 470 atm. the mixtures are less compressible than either of the constituent gases. L. L. Bircumshaw.

Relation between viscosity and the constitution of hydrocarbons of high mol. wt. G. Hugel (Chim. et Ind., 1931, 26, 1282—1288).—The viscosity of cyclic hydrocarbons is greater than that of paraffins of equal mol. wt. The introduction of side-chains to acyclic hydrocarbons has little or no influence on the viscosity; the introduction of Me into cyclic hydrocarbons has a sp. effect, although not always in the same direction. Non-saturation has scarcely any effect on the viscosity of acyclic hydrocarbons, but the viscosity of unsaturated cyclic hydrocarbons is increased by saturation. In any series the max. viscosity appears to be attained by the saturated cyclic hydrocarbon. E. S. Hedges.

Theory of the viscosity of liquids. E. L. Lederer (Kolloid-Beih., 1931, 34, 270—338).—From thermodynamic considerations a formula for the dependence of the viscosity of a pure liquid on temp. has been deduced, and, by reference to the data for more than 160 liquids, is shown to represent their behaviour with considerable accuracy. The following deductions were also made: the crit. kinematic viscosity is practically the same for all liquids; the heat of association is an accurate measure of mol. association and its variation with temp.; the Trouton–Pictet rule is valid for the association of liquids which are not associated in the vapour phase; the internal pressure of liquids and solids can be calc.; there is at least a qual. connexion between viscosity, constitution, mol. cohesion, and dipole moment. A formula connecting pressure and viscosity has also been obtained, and agrees well with the data for a number of liquids, even including H_2O. The theoretical basis of Arrhenius' empirical formula for the viscosity of "ideal mixtures" and the quant. deviations from this formula by "real mixtures" are given. The heat of mixing can be calc. if no other change of internal energy, such as hydration energy, is involved. It is probable that the theory can also be applied to solutions of electrolytes. M. S. Burr.

General equations of energy and entropy of gases. T. C. Huang (Sci. Rep. Nat. Tsing Hua Univ., 1931, **1**, 93—102).—A more detailed account of work already noted (A., 1931, 793).

Viscosity of gases at high pressures. Viscosity of nitrogen to 1000 atm. A. Michels and R. O. Gibson (Proc. Roy. Soc., 1931, **A**, **134**, 288—307).—Details are given of a transpiration method by means of which results are obtained for the viscosity of N_2 at 25°, 50°, and 75° up to 1000 atm. L. L. Bircumshaw.

Aluminium–manganese system of alloys. A. J. Bradley and P. Jones (Phil. Mag., 1931, [vii], **12**, 1137—1152).—*X*-Ray powder photographs show the existence of Al_7Mn, Al_3Mn, a range of solid solutions with 50—60% Mn, and solid solutions of Al in α- and β-Mn. No indication of Mn_3Al was found. The solution of Al in β-Mn lowers the α–β transition point so much that the β-lattice becomes stable at room temp. H. J. Emeléus.

Alloys of zinc and manganese. N. Parravano and V. Caglioti (Atti R. Accad. Lincei, 1931, [vi], **14**, 166—169).—*X*-Ray spectra for alloys containing up to 33·06% Mn show the existence of γ-, ε-, and η-phases analogous with those of brass. The hexagonal ε-phase is stable between 33% and 24% Mn at room temp., and between 24% and 12·5% Mn at higher temp. The γ-phase exists between 22·26% and 8·09% Mn and has a body-centred cubic lattice with 52 atoms in the unit cell. The η-phase consists of solid solutions of about 1% Mn in Zn, but is unstable. O. J. Walker.

***X*-Ray study of alloys of silver with bismuth, antimony, and arsenic. II.** S. J. Broderick and W. F. Ehret (J. Physical Chem., 1931, **35**, 3322—3329; cf. A., 1931, 1223).—*X*-Ray examination of the system Ag–As substantially confirms Heike and Leroux's thermal diagram (A., 1916, ii, 248). Whereas Ag is practically insol. in As, Ag dissolves about 5% of As, the lattice parameter increasing from 4·076 to 4·080 Å. At higher temp. there is formed a β-phase with about 7·5% As, and having the hexagonal close-packed structure. The axial ratio is 1·633 and the side of the unit cell 2·891 and the height 4·722 Å. The crystal structures met with in the Ag–As, Ag–Sb, Ag–Bi, and related systems are discussed. I. J. Patton (c).

Complex systems with iron. IV. System chromium–carbon (and iron–chromium–carbon). E. Friemann and F. Sauerwald (Z. anorg. Chem., 1931, **203**, 64—74).—Equilibria in the systems Cr–C and Fe–Cr–C have been investigated. The existence of Cr_7C_3 is very probable, although the formula Cr_5C_2 is a possible alternative. The solubility of C in solid Cr is less than 0·03%. The m. p. of Cr is lowered greatly by the presence of N. The formation of nitride begins at 1000°. E. S. Hedges.

Internal friction of molten metals and alloys. IV. Internal friction of silver and silver–copper alloys. W. Radecker and F. Sauerwald (Z. anorg. Chem., 1931, **203**, 156—158).—The internal friction of molten Ag–Cu alloys is related linearly to the composition. E. S. Hedges.

Solid solutions between alkali halides. A. Baroni (Atti R. Accad. Lincei, 1931, [vi], **14**, 215—217).—*X*-Ray examination by the Debye method shows that KCl and KI are not miscible in the solid state. *X*-Ray data for the systems KCl–KBr and KBr–KI show that true equilibrium is reached if the mixtures are obtained from solutions. O. J. Walker.

Viscosity of mixtures of tin tetrachloride with aromatic hydrocarbons. I, II. F. De Carli (Atti R. Accad. Lincei, 1931, [vi], **14**, 120—124, 200—205).—I. The viscosities of 0—100% mixtures of PhMe with $SnCl_4$ have been measured at 20° and 30°. PhMe differs from C_6H_6 in its tendency to form association complexes with $SnCl_4$; no definite compound is indicated, however.

II. The viscosities of mixtures of *m*-xylene and of *ψ*-cumene with $SnCl_4$ have been determined at 20° and 30°. The data suggest that C_6H_6 homologues associate with $SnCl_4$ at room temp. The association is almost destroyed, however, at 30°. O. J. Walker.

Partial pressure isotherms. I. W. D. Bancroft (J. Physical Chem., 1931, **35**, 3160—3185).—Association, dissociation, and heat effects resulting from dilution and solvation increase the apparent mol. wt. of one component and lower that of the other except when combination is in an equimol. ratio. A tendency to form two liquid layers increases the partial pressures and apparent mol. wts. of both components, but in all the systems studied the increase is negligible in very dil. solutions and important only in conc. solutions. MeOH, EtOH, and PrOH in H_2O and in C_6H_6, and EtOH in PhMe show abnormally high mol. wts. for both components. In C_6H_6 the order of apparent polymerisation is MeOH>EtOH>PrOH, whereas in H_2O it is the reverse. The true polymerisation coeff. of liquid H_2O, MeOH, and EtOH is less than 2. In the system H_2O–glycerol the deviations of the H_2O isotherm from the ideal curve are small and negative. Addition of anhyd. $CaCl_2$ or NaI separates MeOH–C_6H_6 solutions into two liquid layers, but does not separate EtOH–C_6H_6 solutions. In the system $COMe_2$–MeOH the tendency to form two liquid layers is not the chief cause of anomalous behaviour. R. H. Cherry (c).

System water–ethyl alcohol–acetic acid–ethyl acetate. Mion (Compt. rend., 1931, **193**, 1330—1333).—The limiting compositions of ternary mixtures of (1) H_2O, EtOH, and EtOAc, and (2) H_2O, AcOH, and EtOAc are recorded; data for the quaternary mixtures are also given. C. A. Silberrad.

Solubility of oxygen in iron. H. Esser (Z. anorg. Chem., 1931, **202**, 73—76).—Microscopical examination of specimens of Fe containing O_2, after quenching from temp. between 950° and 1200°, shows that the solubility of O_2 in solid Fe is very small, $<0·02\%$. This result agrees with previous calculations (A., 1931, 1128). The O_2 dissolved in the molten metal separates probably as FeO, which also is very sparingly sol. in Fe. H. F. Gillbe.

Solubility of lithium chloride in water. J. A. N. Friend and A. T. W. Colley (J.C.S., 1931, 3148—3149).—Data are given from 0° to 95°. The transition point $LiCl,2H_2O \rightleftharpoons LiCl,H_2O$ occurs at about 18°. D. R. Duncan.

Solubility of iodine in aqueous salt solutions. A. von Kiss and A. Urmánczy (Z. anorg. Chem., 1931, **202**, 172—190).—The solubility of I in various K, Na, Li, Mg, Ca, and Ba salt solutions has been determined. In absence of KI the solubility in nitrate and sulphate solutions diminishes with increase of the salt concn., whilst in chloride solutions it increases to a max. at about 0·3—0·4*N* and then diminishes. In presence of KI (0·025*N*) the solubility falls continuously with increasing salt concn. The difficulty of calculating the thermodynamic equilibrium consts. of the complex iodide ions is discussed. The vals. of the equilibrium const., expressed in terms of activities, the activity of I', and the ratio of the activities of I_3' and I', have been calc. H. F. Gillbe.

Solubility of calcium hydroxide in aqueous salt solutions. J. Johnston and C. Grove (J. Amer. Chem. Soc., 1931, **53**, 3976—3991).—The solubility at 25° in H_2O is 19·76 millimol. per 1000 g. In solutions of LiCl, NaCl, KCl, CsCl, $SrCl_2$, $BaCl_2$, NaBr, KBr, NaI, $NaNO_3$, $NaNO_2$, $NaClO_3$, $NaClO_4$, and NaOAc the solubility passes through a max. with increasing salt concn., except for $BaCl_2$, and then decreases to a val. which is sometimes less than that for pure H_2O. L. P. Hall (c).

Germanium. VIII. Germanium dioxide. R. Schwarz and E. Huf (Z. anorg. Chem., 1931, **203**, 188—218).—Data for the solubility of GeO_2 in H_2O are discordant. New determinations show that the solubility has no significance unless the ratio GeO_2/H_2O is given. GeO_2 is partly molecularly dissolved and partly colloidally dispersed; the ion $HGeO_3'$ is responsible for peptisation, stabilisation, and dissolution. The crystalloidal portion is supersaturated and gradually diminishes with time. The solubility of GeO_2 is less the higher is the temp. of ignition. Two cryst. forms and one amorphous form have been recognised. The particles of GeO_2 hydrosol are negatively charged and not very stable, tending to

go into true solution (the reverse behaviour of SiO_2 sol). When left undisturbed, the sols separate into periodically-spaced layers having different particle-densities. The dissociation const. of H_2GeO_3 from conductivity measurements is $0{\cdot}5\times10^{-7}$. Dialysis of $NaOH$–GeO_2 mixtures with a cellophane membrane suggests the existence of the ion Ge_5O_{11}''.
E. S. Hedges.

Solubility relations of the isomeric dihydroxybenzenes. W. H. Walker, A. R. Collett, and C. L. Lazzell (J. Physical Chem., 1931, **35**, 3259—3271).—The solubilities in $COMe_2$, Et_2O, EtOH, and H_2O are considerable, but in $CHCl_3$, C_6H_6, and CCl_4 are small. The solubility curves for the *o*- and *m*-isomerides in EtOH, $COMe_2$, and Et_2O fall below the ideal curve deduced from the variation with temp. of the mol. heat of fusion, whereas the solutions in the non-polar solvents deviate in the opposite direction; with H_2O the deviations are only slight. The solubility curve of quinol in $COMe_2$ exhibits a discontinuity at 62° and 33 mol.-%, and compound formation is said to be indicated. C. T. Snell (*c*).

Rhythmic precipitation of stearic acid from alcoholic and ethereal solutions. A. Kutzelnigg (Kolloid-Z., 1931, **57**, 292—293).—Stearic acid crystallises from hot EtOH solution (100 g. in 70 c.c.) and from saturated Et_2O solution in concentric ring systems. Spiral forms were also observed. Substances forming periodic crystallisation structures are said to have a high temp. coeff. of solubility. The phenomenon is believed to be caused by the liberation of heat of crystallisation. E. S. Hedges.

Partition of iodine between carbon disulphide and water. G. Herrero (Anal. Fís. Quím., 1931, **29**, 616—620).—The results agree with recorded data.
H. F. Gillbe.

Crystals produced by solidification of a fused substance containing dyes in solution. P. Gaubert (Compt. rend., 1932, **194**, 109—111; cf. A., 1931, 672).—The dyes (1—20%) were added to various easily fusible colourless org. substances capable of considerable undercooling. When crystallisation occurs near the ordinary m. p. the crystals are colourless, but at lower temp. they are coloured, homogeneous, polychroic, and fluorescent in ultra-violet light. Different modifications of the same substance, *e.g.*, vanillin (cf. A., 1923, i, 154), are differently affected as regards tint, rate of change, and relative amount.
C. A. Silberrad.

Activated and van der Waals adsorption of ammonia and of certain other gases. N. W. Taylor (J. Amer. Chem. Soc., 1931, **53**, 4458—4459).—The belief that activated adsorptions and desorptions are fairly general (A., 1931, 1366) is supported by the literature. Catalytic promoters may serve to provide a mechanism for low activation energy steps by which hysteresis effects are eliminated.
C. J. West (*c*).

Gaseous adsorption. II. Heat of adsorption curve for hydrogen on platinum. E. B. Maxted and N. Hassid (J.C.S., 1931, 3313—3318).—The heat of adsorption or desorption is almost const., irrespective of the amount of H_2 already adsorbed.
D. R. Duncan.

Relative adsorbability of acids by activated carbon and the mass effect of the adsorbents. S. Roychoudhury (Kolloid-Z., 1931, **57**, 308—311).—Deviations from the adsorption isotherm in the adsorption of various acids by C (particularly from sugar) are recorded. The adsorption of a series of org. acids bears no relation to the relative solubilities or dissociation consts. In many cases the curves cut each other. E. S. Hedges.

Hydrolytic adsorption by activated carbon. S. Roychoudhury and J. N. Mukherjee (Kolloid-Z., 1931, **57**, 302—307).—Activated C, prepared in different ways, acquires an increasingly positive charge with repeated washing. Negatively-charged animal charcoal adsorbs alkali but not acid, whilst the positively-charged material adsorbs both. $H^{\cdot}$, OH', Cl', and SO_4'' can all be adsorbed at the solid side of the interface. E. S. Hedges.

Activated charcoal. S. Roychoudhury and J. N. Mukherjee (Z. physikal. Chem., 1931, **157**, 435—441).—Frumkin's theory of the adsorption of electrolytes by activated charcoal is criticised on the basis of an investigation of the charge on the charcoal.
R. Cuthill.

Activated charcoal. A. Frumkin, R. Burstein, and P. Lewin (Z. physikal. Chem., 1931, **157**, 442—446).—Objections to the gas electrode theory of the adsorption of electrolytes by activated charcoal (cf. preceding abstract) are refuted. R. Cuthill.

Discontinuities in adsorption isothermals. A. J. Allmand and L. J. Burrage (J. Amer. Chem. Soc., 1931, **53**, 4453—4454).—The hypothesis of Benton and White (A., 1931, 1005) regarding discontinuities in adsorption isotherms is discussed.
C. J. West (*c*).

Kinetics of adsorption processes. A. R. Ubbelohde and A. Egerton (Proc. Roy. Soc., 1931, A, **134**, 512—523).—The adsorption of H_2 on charcoal at the temp. of liquid O_2 has been studied by an improved and accurate dynamic method. The rate of establishment of equilibrium on desorption is very high. The difference in the viscosities of 50% and 75% mixtures of *o*- and *p*-H_2 is less than 0·3%. The influences of the rotational state of the adsorbed mols. on the discontinuities in the isotherm and the adsorption potential are discussed.
L. L. Bircumshaw.

Adsorption of ions, particularly of radio-elements and dyes, by salt-like compounds. K. Fajans and T. Erdey-Grúz (Z. physikal. Chem., 1931, **158**, 97—151).—The adsorption of positively-charged dye ions by Ag halides is increased by a negative charge on the adsorbent, and diminished by a positive charge; negatively-charged dye ions show the reverse behaviour. Adsorption may, however, occur even if the adsorbent is uncharged, or has a charge of the same sign as that on the adsorbate. In a group of anions of similar constitution the adsorbability of the various ions runs parallel with the smallness of the solubility of the compounds which they form with the $Ag^{\cdot}$ of the adsorbent (cf. A., 1921, ii, 386). The adsorption of Th-$B^{\cdot\cdot}$ from solution in dil. HNO_3 by various Ag salts and the effect of added electrolytes have been studied. Adsorption of the anion of the electrolyte leads to increased adsorption of Th-$B^{\cdot\cdot}$, whereas adsorption of the cation has the reverse effect. Th-$B^{\cdot\cdot}$ is adsorbed by Ag salts even when the adsorbent is free from excess of either of its ions or positively charged by excess of $Ag^{\cdot}$. The adsorbability of $Pb^{\cdot\cdot}$ and IO_3' is greater on $AgIO_3$ than on AgBr. The results show that Fajans' adsorption rule (A., 1913, ii, 1010) and Hahn's rule (A., 1926, 1092) are not of general applicability. It is probable that the adsorption of ions on salt-like compounds is influenced by the surface area of the adsorbent, the presence of foreign electrolytes (primarily through their effect on the charge of the surface), the solubility of the compound of the ion being adsorbed with the oppositely-charged ion of the adsorbent, the relative size and deformability of the ions participating, considerations of isomorphism, and by whether the ions being adsorbed are those of a radioactive element present in minute concn. or are ions of other elements present in weighable amount. In general a salt-like adsorbent free from excess of either of its ions readily adsorbs an ion from aq. solution only if that ion forms with the oppositely-charged ion of the adsorbent a sparingly sol. or only slightly dissociated compound. Further, the adsorption of an ion is increased by the adsorption of another ion with charge of opposite sign and reduced by adsorption of an ion with charge of the same sign. R. CUTHILL.

Chemical and electrical processes at metal surfaces charged with gas. R. SUHRMANN (Z. anorg. Chem., 1931, **203**, 235—244).—A discussion of published work on the effect of mol. layers of gases on the thermoelectric and photo-electric emission of metals, and the relation to heterogeneous catalysis. E. S. HEDGES.

Surface activity of salts of the higher fatty acids. A. LOTTERMOSER and W. TESCH (Kolloid-Beih., 1931, **34**, 339—372).—The variation of surface tension with concn. for solutions of Na salts of higher fatty acids has been studied at 20° and 65°. At 65° a min. is obtained which appears at a lower concn. as the no. of C atoms in the acid increases. Addition of free fatty acid also lowers the concn. of min. σ. The vals. obtained depend on the previous treatment of the solution, especially at 20°. The addition of NaOH or Na_2CO_3 at 60° increases the surface tension and alters the form of the concn.-σ curve. There is no appreciable adsorption of soap by added lamp-black. M. S. BURR.

Slippage in a non-Newtonian liquid. M. REINER (J. Rheology, 1931, **2**, 337—350).—A 1·71% solution of cellulose nitrate in Bu phthalate is a non-Newtonian liquid which appears to slide on a glass wall. The fluidity increases with the age of the solution. This type of system is treated mathematically. E. S. HEDGES.

Quasi-laminar capillary flow. R. L. PEEK, jun., and W. R. ERICKSON (J. Rheology, 1931, **2**, 351—369).—A mathematical treatment of the physical conditions under which flow through capillaries may be steady and yet not parallel to the axis of the tube. The conclusions reached do not account for all the anomalies observed in the viscosity of colloidal solutions, and it is suggested that mol. orientation may be involved. E. S. HEDGES.

Dynamics of membrane permeability in relation to ion-distribution. S. K. LIU (Kolloid-Z., 1931, **57**, 285—292).—Mathematical. E. S. HEDGES.

Ultrafiltration. I. Ultrafiltration of electrolytes from alkali caseinogenate solutions. D. M. GREENBERG and M. GREENBERG (J. Biol. Chem., 1931, **94**, 373—382).—Data showing the electrolyte concn. in filtrates from mixtures of alkali caseinogenate with corresponding inorg. alkali salts support the view that a Donnan membrane equilibrium is involved in their ultrafiltration. A. COHEN.

Osmosis in systems containing liquids of constant composition. V. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 823—830; cf. A., 1931, 795).—Mathematical. W. R. ANGUS.

Specific permeability of capillary systems. E. MANEGOLD and R. HOFMANN (Biochem. Z., 1931, **243**, 51—66).—The sp. permeability of a capillary system is discussed and the vals. for a collodion membrane are determined by the use of H_2O and aq. solutions of capillary-active substances. The vals. vary with the nature of the dissolved substance. The mechanism of the action of permeability regulators is discussed. P. W. CLUTTERBUCK.

Electrostatic explanation of the phenomenon of flotation. B. KAMIENSKI (Nature, 1932, **129**, 59—60).—The potential of unattackable electrodes such as Pt, PbS, and Acheson graphite is reduced when the electrodes are wetted by an emulsion of dielectrics in H_2O. Zn electrodes, not being inert, change their potential but little. L. S. THEOBALD.

Electrocapillary curves of mixtures of normal alcohols with water, and adsorption of alcohol molecules at mercury surface. C. OCKRENT (J. Physical Chem., 1931, **35**, 3354—3366).—The curves for the complete series of mixtures of MeOH, EtOH, and PrOH with H_2O and some BuOH–H_2O mixtures have been measured. The calc. areas of alcohol mols. at the p.d. where max. adsorption occurs agree fairly well with those calc. from insol. alcohol films on H_2O. Up to fairly high concns. the alcohols appear to form a unimol. layer at the charged Hg surface, and are oriented in the same way as at the air–H_2O interface. In solutions of various alcohols H_2O appears to raise the interfacial tensions at polarisations more positive than $-0{\cdot}6$ volt and lower them at more negative polarisations. These effects may be ascribed to large liquid junction potentials or to a positive adsorption of H_2O at negative polarisations, which increase as the homologous series is ascended. F. L. BROWNE (*c*).

Kinetics of coagulation at boundary surfaces. H. FREUNDLICH and R. VON RECKLINGHAUSEN (Z. physikal. Chem., 1931, **157**, 325—341).—The mechanical coagulation, *i.e.*, coagulation by stirring, of a CuO sol occurs at the liquid–gas interface, since it does not take place if the stirring is such that the surface of the liquid is not disturbed or renewed. When the sol is stirred in a similar way with 1-

bromonaphthalene or Hg, the first result is the formation of an emulsion stabilised by the CuO, and the rate at which CuO is removed from the sol changes as stirring proceeds. Ultimately, however, mechanical coagulation at an approx. const. rate starts at the Hg–H_2O interface. R. Cuthill.

Alkali aluminium silicates. II. Ammonium permutites and their derivatives and an attempted chemical classification of the permutites. III. Hydrolysis of permutites. E. Gruner [in part with E. Hirsch] (Z. anorg. Chem., 1931, **202**, 337—357, 358—371).—II. Cation exchange has been studied in the permutites of the type $m Na_2O,nAl_2O_3,pSiO_2,qH_2O$, where $m:n:p:q=$ 1 : 1 : 2 : 2, 1 : 1 : 3 : 4, and 1 : 1 : 4 : 4. With these, NH_4Cl yields respectively

$0{\cdot}5(NH_4)_2O,Al_2O_3,2SiO_2,2{\cdot}5H_2O$ (*A*),

$(NH_4)_2O,Al_2O_3,3SiO_2,5H_2O$ (*B*), and

$(NH_4)_2O,Al_2O_3,4SiO_2,5H_2O$ (*C*). N_2H_4,HCl gives similar products. *B* and *C* behave normally with NaCl, but *A* gives rise to $0{\cdot}5Na_2O,Al_2O_3,2SiO_2,2{\cdot}5H_2O$, whereas it forms the original permutite with NaOH. N_2H_4 is eliminated from N_2H_5-permutites by H_2O_2, which forms a mol. compound in which H_2O_2 can be replaced by H_2O, NH_3, or SO_2. By treatment in a sealed tube with excess of NaOH permutites with more than 2 mols. of SiO_2 are converted into the 1 : 1 : 2 : 2 type. The reactions observed can best be explained by considering the simplest permutite to be a salt of the dibasic acid $[Al_2Si_2H_4O_{10}]H_2$, the permutites with higher proportions of SiO_2 being regarded as solid solutions of the parent substance with H_4SiO_4 or H_2SiO_3.

III. When Ag-permutites of the simplest type are treated with dil. K_2CrO_4, the solid is coloured red and contains CrO_4'' in excess of the amount corresponding with the observed cation exchange. With excess of K_2CrO_4 the cation exchange is complete, and the Ag_2CrO_4 formed remains attached to the permutite. This and other similar reactions are attributed to hydrolysis of the permutite, which has been directly measured, and amounts, under the conditions used, to 33%. F. L. Usher.

Examination of protein films. A. Hughes, J. Schulman, and E. K. Rideal (Nature, 1931, **129**, 21).—Proteins such as egg-albumin, gliadin, and glutenin can be made to spread in the form of highly-dispersed, uniform films on the surface of H_2O by the method described. Preliminary results of the examination of aq. protein systems by the method of surface potentials are described. L. S. Theobald.

Association of aromatic nitroso-compounds in solution. D. L. Hammick [with W. S. Illingworth, W. A. M. Edwards, and (Miss) E. Ewbank] (J.C.S., 1931, 3105—3111).—Mol. wts. in C_6H_6 have been determined cryoscopically. PhNO and its *m*- and *p*-derivatives are only slightly associated (mean= 2·3% bimol.), but *o*-substitution favours association (mean for di-*o*-derivatives=61·9%). Probably a dipole aggregate is first formed and this passes over into an oxyazoxy-structure. D. R. Duncan.

Action of boric acid and borates on rotatory power of glucose, galactose, and fructose. E. Darmois and (Mlle.) R. Peyroux (Compt. rend., 1931, **193**, 1182—1185).—The variations in rotatory power of solutions containing glucose and a Na borate (cf. A., 1930, 69) increase with the alkali content of the borate. With $NaBO_2$ [α] first diminishes, becoming negative, passes through a min., and then rises to a limiting val., whilst the dispersion increases; the velocity of the changes increases with rise of temp. It is inferred that a lævorotatory complex of borate and glucose, probably $Na_2[(BO_2)_2,C_6H_{12}O_6]$, is formed, the changes in [α] being due to variations in the relative amounts of this and of glucose. At 20° $K=$[glucose][borate]/[complex]$=0{\cdot}21$. Similar results were obtained with galactose and fructose. C. A. Silberrad.

Influence of electrolytes on the dielectric constant of water. I. Experimental method. II. Uni-univalent salts. R. T. Lattey and W. G. Davies (Phil. Mag., 1931, [vii], **12**, 1111—1136).—The dielectric const. of aq. solutions of KCl, NaCl, NaF, and $NaIO_3$, determined by the voltage tuning method, is greater than that of H_2O. The increase is proportional to the concn. of dissolved salt, and is the same for equiv. concns. of each uni-univalent salt examined within the error of experiment. H. J. Emeléus.

Viscosity of dilute solutions of strong electrolytes. W. E. Joy and J. H. Wolfenden (Proc. Roy. Soc., 1931, **A**, **134**, 413—427).—The viscosities of aq. solutions of KCl, $KClO_3$, $RbNO_3$, and HNO_3 (concn. range *N*—0·002*N*) have been measured at 18°, and in all cases, in agreement with the theory of Jones and Dole (A., 1929, 1385), the viscosity is greater than that of H_2O. The Falkenhagen–Dole theory (A., 1929, 1389) is confirmed by the limiting slopes of the viscosity–concn. curves and their temp. coeffs. L. L. Bircumshaw.

Two varieties of aqueous solutions of a cobaltous salt: relation of magnetic state to concentration. A. Lallemand (Compt. rend., 1931, **193**, 1323—1325).—The solutions of $CoCl_2$ with const. (*a*) and variable (*b*) magnetic susceptibility described by Trümpler (Diss., Zürich, 1917), are obtained (*a*) by preventing contact between the dissolving crystals ($CoCl_2,6H_2O$) and conc. solution, *e.g.*, by continual agitation, and (*b*) by preparing in the first instance a very conc. solution, subsequent dilution having no effect. The magnetic moment of the "variable" solutions is practically independent of the concn., but the Curie point rises from −18° for *C* 0·072 to −7° for *C* 0·0125, the mol. field being thus a function of *C* (cf. A., 1928, 454). C. A. Silberrad.

Colloidal theory of van der Waals gases. S. Ray (Kolloid-Z., 1931, **57**, 259—266).—Theoretical. E. S. Hedges.

Properties of aërosols. S. C. Blacktin (Nature, 1931, **138**, 968). L. S. Theobald.

Theory of the electrification of aërosols. H. S. Patterson (Phil. Mag., 1931, [vii], **12**, 1175—1182).—Calculation shows that for slightly charged aërosols the fraction of particles charged should increase with time, and for aërosols highly charged initially should remain const. Calc. and experimental vals. agree for NH_4Cl, stearic acid smoke, and for MgO from burning Mg. H. J. EMELÉUS.

Highly polymerised compounds. LVII. Viscosity measurements with solutions of long thin molecules. H. STAUDINGER and E. OCHIAI (Z. physikal. Chem., 1931, **158**, 35—55; cf. A., 1930, 571).—At 20° the sp. viscosity (relative increase in viscosity caused by the solute), η_{sp}, of CCl_4 solutions of long straight-chain paraffins, aliphatic esters, and ketones and C_5H_5N solutions of fatty and dicarboxylic acids is given by $\eta_{sp}/c=ny+x$, where c is the quotient of the concn. in g. per litre by 14 (the mol. wt. of the CH_2 group), n the no. of C atoms in the mol., y a const. characteristic of the CH_2 group, and x a const. which is zero for paraffins but depends on the nature of the group containing O in the other compounds. This equation, which is valid only if n exceeds 9, shows that the solute mols. are long thin structures in the dissolved as in the cryst. state. For CCl_4 solutions of straight-chain fatty acids $\eta_{sp}/c=2ny+x$, indicating that, as in the solid state, the acid mols. are linked end to end in pairs. The introduction of a double linking into a fatty acid scarcely affects η_{sp}/c. Aliphatic esters with straight chains have larger sp. viscosities than isomerides with branched chains. Ring structure markedly increases the viscosity.

R. CUTHILL.

Viscosity of suspensions of elongated particles, and their interpretation by space-filling. R. EISENSCHITZ (Z. physikal. Chem., 1931, **158**, 78—90).—Theoretical. Calculation of the viscosity, η, of a suspension of elongated ellipsoidal particles on lines similar to those followed in Einstein's theory of the viscosity of a suspension of spherical particles has shown that $\eta/\eta_0-1=1{\cdot}15va/\{\pi Vb\ \log_e(2a/b)\}$, where η_0 is the viscosity of the dispersing medium, V the vol. of the suspension, and v the total vol. of the suspended particles, the semi-axes of which are a and b. This equation agrees satisfactorily with the data for the viscosity of solutions of long-chain paraffins (A., 1930, 571). The fact that the viscosity of a suspension deviates from the requirements of Einstein's theory in so far as it depends, not only on v, but also on the nature of the suspended particles does not prove therefore that the dispersed particles occupy a larger vol. than corresponds with their dimensions. R. CUTHILL.

Suspension effect of Wiegner and Palmann. I. Activity of the adsorbed ions. J. M. ALBAREDA Y HERRERA (Anal. Fís. Quím., 1931, **29**, 643—650).—The variation of the suspension effect in acid and alkaline suspensions of clays with variation of the $p_{\rm H}$ of the disperse medium has been studied, and the activities of the adsorbed ions have been calc.

H. F. GILLBE.

Theory of the micellar state in relation to the idea of complexity in chemistry. G. MALFITANO and M. CATOIRE (Kolloid-Z., 1931, **57**, 266—276).—The micelle is treated as a structural chemical unit in the series: atom, mol., complex mol., micelle.

E. S. HEDGES.

General colloid chemistry. XXV. Dependence of the properties of aluminium hydroxide sols on the colloid equivalent. F. MUTTONÉ and W. PAULI (Kolloid-Z., 1931, **57**, 312—324).—The colloid equiv. is the no. of mols. corresponding with a single free charge of the oppositely-charged ion. The colloid equiv. of $Al(OH)_3$ sols is increased by boiling, whilst the viscosity increases and the activity coeff. of the oppositely-charged ion (Cl') decreases strongly. The changes are caused by the formation of secondary particles. With increasing colloid equiv. the electrophoretic velocity falls to a min. and then slowly rises; the viscosity behaves similarly. The activity coeff. of Cl' falls steadily as the colloid equiv. is reduced. There is a relation between viscosity and the free charge. The flocculation vals. of egg- and serum-albumin are low for small colloid equivs., but increase markedly and later fall as the colloid equiv. increases. E. S. HEDGES.

Diffusion in alkaline copper solutions. V. L. RICKETTS and J. L. CULBERTSON (J. Amer. Chem. Soc., 1931, **53**, 4002—4008).—Equations giving rates of diffusion for certain boundary conditions are deduced and utilised to distinguish between colloids and complexes in certain alkaline hydroxy-org. Cu systems. The diffusion coeff. of the glycerol–Cu complex into agar gel is comparable with those of many crystallisable salts. R. H. CHERRY (c).

Migration studies with ferric oxide sols. II. Negative sols. F. HAZEL and G. H. AYERS (J. Physical Chem., 1931, **35**, 3148—3159; cf. A., 1931, 1232).—The conversion of positive Fe_2O_3 sols into negative sols by means of $K_4Fe(CN)_6$ is related to the $p_{\rm H}$ of the medium. The sols lose their stability when the particles migrate with a velocity between about $-2{\cdot}0$ and $+2{\cdot}0\ \mu$ per sec. per volt per cm., vals. which correspond with the crit. potentials. The isoelectric point of the sol is not determined uniquely by its $p_{\rm H}$. The effect of $K^{\cdot}$, $Ba^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, and $Th^{\cdot\cdot\cdot\cdot}$ on the migration velocity of negative sols is illustrated. F. SAUNDERS (c).

Flow of colloids which show anomalous viscosity. H. KROEPELIN (J. Rheology, 1931, **2**, 385—391).—Measurements of the distribution of velocity of flow of colloidal solutions at different points in a tube of circular cross-section indicate that the properties of solids play no important part in the anomalies. E. S. HEDGES.

Highly-polymerised compounds. LVIII. Streaming double refraction of protein solutions. G. BOEHM and R. SIGNER (Helv. Chim. Acta, 1931, **14**, 1370—1403).—The applicability of streaming double refraction measurements to the investigation of mol. aggregation has been studied. In ordinary colloidal solutions streaming anisotropy is caused principally by the orientation of elongated particles, which may be either mols. or micelles. Proteins may be classified according to the form of the mols. in solution, as indicated by refraction measurements: in solutions of ovalbumin and myogen the particles are spherical, and in solutions of myosin elongated, whilst in solutions of ovoglobulin they form long threads; gelatin solutions appear to contain short rod-shaped particles. Deformation of the particles as a consequence of reaction may be detected by the measurements, but no evidence in support of

Meyer's theory of muscular contraction is afforded by measurements with ovoglobulin and polyacrylic acid. H. F. Gillbe.

Inactivation, viscosity, and p_H value of gum arabic solution. S. A. Schou and J. M. Olsen (Dansk Tidsskr. Farm., 1932, 6, 6—16).—The viscosity shows a nearly const. max. between p_H 4 and 10; above and below these limits it decreases rapidly (cf. A., 1928, 706). The addition of 0·5% of "nipagin" has no effect on the viscosity. The viscosity decreases if the solution is heated at 100° for 30 min., and the acidity increases slightly at the same time, but there appears to be no definite relation between the two. The decrease in viscosity on heating is not merely transitory, as out of 5 samples only 2 showed a slight subsequent increase again after 14 days. The use of gum arabic solution as a protective colloid in the prep. of a camphor suspension has been studied. H. F. Harwood.

Solutions of cellulose [derivatives]. J. Duclaux and F. Hirata (J. Chim. phys., 1931, 28, 537—545).—Solutions of cellulose in $Cu(NH_3)_4(OH)_2$, cellulose nitrate in $COMe_2$, $PhNO_2$, $C_5H_{11}\cdot OAc$, or COMeEt, cellulose trinitrate in COMeEt, cellulose acetate in $COMe_2$, and cellulose triacetate in $C_2H_2Cl_4+EtOH$ have no measurable permanent rigidity, although the viscosity of some of these solutions is 10^7 times that of H_2O. The time of relaxation of 6% cellulose nitrate in $PhNO_2$ is 170 sec.

E. S. Hedges.

Concentrations at which coagulative power of certain organic substances is maximal. B. Jirgensons (Z. physikal. Chem., 1931, 158, 56—64).—The coagulative action of PhOH, $COMe_2$, and various alcohols on starch and egg-albumin sols rises with increasing concn. of coagulant, and attains a max. at a concn. which is a linear function of the dielectric const. of the coagulant and increases with it. The max. is sometimes followed by a min.

R. Cuthill.

Periodic precipitation in the absence of colloids. J. W. McBain (Nature, 1931, 128, 1042).—Attention is directed to the work of Morse and Pierce (A., 1904, 14; 1930, 1117) in which periodic pptn. in the absence of a gel has been observed.

L. S. Theobald.

Spiral precipitation. (Mlle.) S. Veil (Compt. rend., 1931, 193, 1337—1339).—The method previously described (cf. A., 1930, 1516) occasionally gives rise to spirals, in which case log (distance between successive spirals measured along a radius vector from centre of drop) varies linearly with the ordinal no. of the spiral (cf. A., 1914, ii, 631; 1930, 1117). C. A. Silberrad.

Analogue of the acclimatisation phenomenon in the protection of arsenious sulphide sol by gelatin. A. J. Rao (J. Indian Chem. Soc., 1931, 8, 621—622).—When gelatin is added drop by drop to As_2S_3 sol, the protected sol is less stable towards electrolytes than when the protective colloid is added rapidly. E. S. Hedges.

Pectography and the constitution of colloidal solutions. E. S. Hedges (Chem. and Ind., 1932, 25—26).—The work of Bary (A., 1928, 705, 1186, *et seq.*) on the deposits produced by the desiccation of colloidal solutions of metallic hydroxides and sulphides, and dyes is discussed. The production of banded deposits is explained in terms of Hedges' general theory of the formation of periodic structures (A., 1930, 1261). The crit. condition is provided by the free electrolyte in the colloidal solution, which, by evaporation in the surface, reaches a concn. at which it coagulates the colloid. Successive bands of deposit are formed each time the concn. of electrolyte reaches the crit. val. for coagulation.

E. S. Hedges.

Colloid chemistry of gliadin separation phenomena. H. L. B. De Jong and W. J. Klaar (Trans. Faraday Soc., 1932, 28, 27—68; cf. B., 1930, 31, 787; 1931, 177).—The separation is continuous and there is no evidence that a crit. charge of the particles is involved. The relative viscosity, η, of aq. sols at 25° increases with concn. of EtOH and $COMe_2$ to a max. with 48 vol.-% and 44 vol.-%, respectively, and the difference in relative viscosity in the presence of equiv. quantities of univalent electrolytes is almost zero at these max., where a reversal of the lyotropic series occurs. The vals. of η for 44% $COMe_2$ sols decrease with increasing concn. of uni- and bi-valent ions. The small differences between vals. of η for 44% $COMe_2$ sols containing equimol. concn. of KCl and KI increase with protein concn., and for const. protein concn. the differences increase with concn. of salt until the sol is discharged. The difference is max. with sols of max. viscosity and min. at the isoelectric point as well as with higher $[H^{\cdot}]$.

The results are interpreted on the assumption that ionic adsorption influences the boundary potential and mol. adsorption causes the lyotropic effects. The latter in certain EtOH and $COMe_2$ media is the same, or zero, for electrolytes of the same valency.

J. G. A. Griffiths.

Relation of proteins to colloids and electrolytes. W. Pauli (Naturwiss., 1932, 20, 28—37).—A lecture.

Swelling. IV. Adsorption of hydrochloric acid by hide and the related swelling. A. Lottermoser and H. Thiele (Kolloid-Z., 1931, 57, 343—353; cf. A., 1931, 1232).—The adsorption of HCl by cowhide (deprived of hair) is reversible, but the accompanying swelling is partly irreversible. The liquid inside the hide is not pure H_2O, but has the same composition as the surrounding swelling liquid. This fact must be considered in adsorption measurements.

E. S. Hedges.

Swelling of pine-wood cellulose through electrolytes and organic substances in aqueous solution. C. G. Schwalbe and O. Fischer (Kolloid-Z., 1931, 57, 338—343).—The swelling of pine-wood cellulose in H_2O is increased by alkalis and decreased by acids. Small amounts of alcohols or $COMe_2$ increase the swelling, but further quantities have no further effect. Carbohydrates and NH_2-acids increase the swelling in proportion to their concn.

E. S. Hedges.

Hydrogels. XI. System SiO_2–H_2O. XII. System SnO_2–H_2O. A. Simon and P. Rath (Z.

anorg. Chem., 1931, **202**, 191—199, 200—204).—XI. A method is described for the determination of the v. p.–temp. curves of hydrated SiO_2, prepared by the action of HCl on hydrated Na silicate at low temp.; if anhyd. acid is used, anhyd. SiO_2 is formed immediately, and it is necessary to have sufficient H_2O present to form a hydrate of HCl. The decomp. isobars show the existence of $SiO_2,2H_2O$, $SiO_2,1{\cdot}5H_2O$, and SiO_2,H_2O; $SiO_2,0{\cdot}5H_2O$ probably exists, but there is no evidence of $SiO_2,2{\cdot}5H_2O$.

XII. Similar measurements with the product obtained by the action of 98% HNO_3 on Na stannate demonstrate the existence of $SnO_2,3H_2O$ and SnO_2,H_2O; the heats of formation of these compounds are about 15·5 and 30 kg.-cal., respectively, compared with 14 and 26·5 kg.-cal. for $SiO_2,2H_2O$ and SiO_2,H_2O, respectively. The results are compared with those for other elements of the fourth group.

H. F. GILLBE.

Difference between the *X*-ray spectra of gelatin sol and gelatin gel. J. R. KATZ, J. C. DERKSEN, and W. F. BON (Rec. trav. chim., 1931, **50**, 1138; cf. A., 1931, 971).—*X*-Ray spectra of a conc. gelatin–H_2O mixture at 55° (sol) and at 20° (gel) are reproduced.

C. W. DAVIES.

Influence of organic substances on the formation of jellies of thorium arsenate, phosphate, and molybdate. S. PRAKASH (Z. anorg. Chem., 1931, **201**, 301—313; cf. A., 1929, 1235).—Gelatinisation of all three substances is retarded by glycerol and accelerated by carbamide. The action of glycine is sp. The results are discussed.

F. L. USHER.

Rôle of cations in the gelation of pectin sols. S. GLÜCKMANN (Kolloid-Z., 1931, **57**, 330—338).—Determinations of ash and OMe content, p_H, viscosity, particle size, and gelation under the influence of the chlorides of Li, Na, K, Mg, Ca, Ba, and Al have been made with pectin sols. The tendency to gelate depends on the valency and degree of hydration of the cation. The results support the crystallisation theory of gelation.

E. S. HEDGES.

Ageing phenomena of chromic hydroxide gel. K. KLANFER and F. PAVELKA (Kolloid-Z., 1931, **57**, 324—330).—The course of ageing of gelatinous $Cr(OH)_3$ has been followed by determining its solubility in AcOH, $H_2C_2O_4$, H_3BO_3, oleic acid, and KOH. The solubility was found to decrease steadily with age. There is a discontinuity between 50° and 80°, and the H_2O content of the gel varies with temp. in a similar way.

E. S. HEDGES.

Thixotropic behaviour of thorium jellies. S. PRAKASH and N. N. BISWAS (J. Indian Chem. Soc., 1931, **8**, 549—555).—The molybdate and phosphate jellies are highly thixotropic, whilst Th arsenate jellies are thixotropic when freshly prepared. The time of thixotropic setting is almost const. for the clear jellies, but with opalescent, agglomerated jellies, such as Th arsenate, it decreases on repetition. The thixotropic time is less than the original time of setting and is greater for dil. jellies than for conc. jellies. The effect of shaking is to set free the structurally-imbibed liquid of the jelly. Glycerol and sucrose act as peptising agents and increase the setting and thixotropic times. Glycine in small quantities decreases the thixotropic time, but has a stabilising influence at higher concns. K_2SO_4 decreases the setting and thixotropic times.

E. S. HEDGES.

Gels. I. Syneresis of silica gel. II. Effect of hydrogen-ion concentration on syneresis of silica gel. D. G. R. BONNELL (Trans. Faraday Soc., 1931, **28**, 1—11, 12—19; cf. A., 1930, 1519).—I. Apparatus for determining the velocity of syneresis and the composition of the exuded liquid is described. At p_H 8 and SiO_2 concn. greater than 5%, the initial velocity and the final vol. of liquid increase with the concn., but below 5% the gels exude increasing quantities of liquid as the concn. falls. For the same p_H and SiO_2 concn., the acid used in the prep. of the gel affects the velocity of syneresis and the vol. of liquid exuded increases in the order AcOH, HCl, H_2SO_4. No change of total vol. accompanies the syneresis of either acidic or alkaline gels. The setting time and the induction period increase with decreasing concn.

II. Gels at p_H between 3 and 11 have been investigated. At the highest p_H vals. the SiO_2 content of the exuded liquid increases with the initial concn. of the gel. The total vol. of liquid exuded is minimal at p_H 8 and increases more rapidly with increase than decrease of p_H. The initial velocity of syneresis is maximal at p_H 8. The setting time and period of induction increase as the p_H recedes in either direction from 8, independently of the acid used. The results indicate an isoelectric point between p_H 7·5 and 8·0 for 6·5—9% SiO_2 gels at 20°. The vol. of liquid exuded increases with rise of temp.

J. G. A. GRIFFITHS.

Preparation and properties of artificial sponges of cellulose. E. HUBERT (Kolloid-Z., 1931, **57**, 253—258).—Photomicrographic examination reveals that the natural sponge is a 3-dimensional network, the rubber sponge is a solid foam, and the viscose sponge is a combination of these forms, the walls of the cells containing capillary pores, whilst the spaces contain a capillary network. The porosity and H_2O-retaining capacity of the viscose sponge vary with the concn. of viscose solution used and with the solubility of the salt added. Viscose sponges shrink considerably (25—40%) on drying, but regain their original vol. in a few sec. in H_2O.

E. S. HEDGES.

Temperature at which unbound water is completely frozen in a biocolloid. J. L. ST. JOHN (J. Amer. Chem. Soc., 1931, **53**, 4014—4019).—From the observation that a temp. of −12·5° is sufficient to freeze all the "free" (freezable) H_2O in a hydrophilic biocolloid, whereas the remaining H_2O ("bound" H_2O) is not frozen at −12·5° to −35°, it is inferred that the average amount of bound H_2O in the thick part of egg-white is about 20%. An improved formula for the calculation of free H_2O is given.

C. J. WEST (*c*).

Theory of the Ludwig–Soret effect. B. BRUŽS (Z. physikal. Chem., 1931, **157**, 422—434).—From thermodynamic considerations and the theory of stationary heat flow it is found that $\sigma = -(1/NT)(\partial\bar{c}_p/\partial N)/(\partial^2\bar{S}/\partial N^2)$, where σ is the Soret coeff. for the component of a solution having the mol. fraction N, $\bar{c}_p$ the partial mol. sp. heat, $\bar{S}$ the partial mol. entropy, and T the temp. For a dil. solution this becomes $\sigma=-(1/RT)\partial\bar{c}_p/\partial \log_e N$, which agrees satisfactorily with available experimental data. The Soret effect proves to be a special case of a general dynamic effect, and is analogous to the Peltier, Seebeck, and Hittorf effects. R. CUTHILL.

Calculation of degrees of dissociation of weak electrolytes. W. H. BANKS (J.C.S., 1931, 3341—3342).—In solving the equation $\alpha=\Lambda/\Lambda_x$, where Λ is the conductivity and Λ_x the sum of the ionic mobilities, Λ_x can be calc. directly from the expression $\Lambda_x=\sqrt{[\Lambda_0{}^2-2b(\Lambda_0\Lambda C)^{\frac{1}{2}}]}$. Here C is the equiv. concn., and b the Onsager slope for the electrolyte. C. W. DAVIES.

Application of Debye's electrolytic theory to concentrated solutions. G. SCATCHARD (Physikal. Z., 1932, **33**, 22—32).—An extension of the Debye–Hückel theory of strong electrolytes to include non-ionic forces. The equation deduced explains variation of osmotic and activity coeffs. A. B. D. CASSIE.

Electrolytic dissociation of acids in salt solutions. III. Dissociation constants of certain acids and activity relations of their ions in sodium and potassium chloride solutions. E. LARSSON and B. ADELL (Z. physikal. Chem., 1931, **157**, 342—362).—Previous investigation (A., 1931, 1368) has been extended to other acids. The substitution of Me, Ph, or OH groups in a normal fatty acid affects the vals. of $-\log\phi$ and $-\log\psi$ only if the substituent is introduced into the α-position. Substitution of OH in the *o*- or *m*-position to the CO_2H group in BzOH has no effect. The vals. of ϕ and ψ for a carboxylic acid depend on the effective radius of the anion, which, whilst it is determined essentially by the CO_2' group, may be affected by the presence in the ion of certain atoms or groups, particularly strongly polar groups, and the more so the nearer these are to the CO_2' group. At the same time, other ions exert an influence: the ions of NaCl and KCl deform the acid anions. R. CUTHILL.

Iodine. J. LANZA (Anal. Fís. Quím., 1931, **29**, 621—642).—Study of solutions and crystals of alkali polyiodides, and of the f.-p. depression, electrical conductivity, transport, absorption spectra, and behaviour towards animal C of aq. solutions of I, suggests that I is not truly sol. in H_2O, but is sol. in, *e.g.*, KI. H. F. GILLBE.

Lead chamber process. I. System nitrosylsulphuric acid–sulphuric acid–water. E. BERL and H. H. SAENGER (Z. anorg. Chem., 1931, **202**, 113—134).—The v. p. of solutions of HSO_5N in 64—80% H_2SO_4 solutions has been determined by a static method at temp. between 30° and 150°. The calc. latent heat of evaporation, λ, of HSO_5N rises from 8223 g.-cal. in 64% H_2SO_4 solution to 12,383 g.-cal. in the 80% acid; there is an abrupt discontinuity in the λ–concn. curve at about 73% H_2SO_4. The v. p. of the solutions is very greatly increased by addition of HNO_3. H. F. GILLBE.

Amphoteric hydrated oxides, their aqueous solutions and crystalline compounds. XIII. Silicic acids and dissolved hydrated silica in alkaline and acid solutions. G. JANDER and W. HEUKESHOVEN (Z. anorg. Chem., 1931, **201**, 361—382; cf. A., 1931, 183).—From data relating to the diffusion and ultra-violet absorption of Na silicate solutions of different p_H, and to the solubility of silicic acid in mineral acids, it is inferred that SiO_3'' exists only when the $[H^{\cdot}]$ is less than that of *N*-NaOH. It is readily hydrolysed to give $2OH'+Si_2O_5''$, which latter is stable between p_H 13·5 and 10·9. At lower p_H silicic acid is largely polymerised and tends to separate from its solutions, the part remaining in true solution being of a more basic character than mono- or disilicic acid. Its conversion into the latter is shown by thermometric or conductometric titration with NaOH. F. L. USHER.

Exceptional isotherm at 0° of the system palladium–hydrogen. L. J. GILLESPIE and J. H. PERRY (J. Physical Chem., 1931, **35**, 3367—3370).—The isotherm is apparently an extension of the normal isotherm into the metastable region. The highest pressure observed was 110 mm., the solid phase containing about 0·95 atom of H per atom of Pd. F. D. ROSSINI (*c*).

Redetermination of thermal dissociation equilibria of inorganic compounds. I. Dissociation equilibrium of calcium carbonate by means of a high-temperature vacuum balance. S. TAMARU, K. SIOMI, and M. ADATI (Z. physikal. Chem., 1931, **157**, 447—467).—Measurements of the dissociation pressure, p, at 614—891° are in good agreement with those of Andrussov (A., 1925, ii, 803). The relation between p and T is given by $\log p=-39{,}670/4{\cdot}575T+10{\cdot}385$, or, more exactly, by $\log p=-9220/T+1{\cdot}70\log T-0{\cdot}00149T+1{\cdot}443\times10^{-7}T^2+7{\cdot}181$. A vac. spring balance utilising a coiled quartz fibre and suitable for high-temp. work is described. R. CUTHILL.

Complex-chemical behaviour of lithium. II. Lithium halides with ethylamine or propylamine. A. SIMON and H. KIMMERLE (Z. anorg. Chem., 1931, **202**, 385—402; cf. A., 1929, 431).—Tensimetric measurements show the existence of the following *compounds* (temp. of decomp. in parentheses): LiCl with 1 (−5°) and 3 (−37°) mols.; LiBr with 1 (59°), 2 (31°), and 4 (−12°) mols.; LiI with 0·5 (135°), 2 (76°), and 4 (22°) mols. NH_2Et; LiCl with 1 (29°), 2 (11°), and 4 (−25°) mols.; LiBr with 1 (69°), 2 (46°), and 4 (4°) mols.; LiI with (128°), 2 (93°), and 4 (38°) mols. NH_2Pr. Heats of formation are calc. and the valency isobars discussed. F. L. USHER.

Fused products of Cr_2O_3–SiO_2 system. Y. YAMAGUCHI and H. NAKAZAWA (Bull. Chem. Soc. Japan, 1931, 6, 285—289).—By fusing together SiO_2 and Cr_2O_3 at 1700—2000°, glasses of various colours are produced. The influence of composition, temp. of fusion, rate of cooling, and reheating on the colour has been investigated and the products have been examined microscopically. D. R. DUNCAN.

Freezing of solutions. VI. Freezing of mixtures of di- and tetra-symmetrically substituted derivatives of ethane. J. TIMMERMANS and (MME.) VESSELOVSKY (Bull. Soc. chim. Belg., 1931, **40**, 504—

517).—The equilibrium in binary mixtures of numerous derivatives of C_2H_6 has been deduced from f. p.–composition curves. Binary mixtures of halogenated derivatives generally form ideal solutions having a simple eutectic when the halogen atoms are identical, but when different halogens are present in the two components mixed crystals are formed. On the other hand, binary mixtures of *s*-di- with tetra-substituted derivatives form equimol. compounds, whether the substituent radicals are halogens or otherwise. A stereochemical explanation of the formation of these compounds is given. E. S. Hedges.

Binary systems comprising carbamide with metallic nitrates. W. J. Howells (J.C.S., 1931, 3208—3212).—Thermal diagrams indicate the existence of the *compounds* $LiNO_3,2CO(NH_2)_2$, m. p. 126°, and $Ca(NO_3)_2,4CO(NH_2)_2$, m. p. 151·5°. No compounds are formed with NH_4NO_3, $NaNO_3$, KNO_3, or $TlNO_3$, but association occurs in solution. D. R. Duncan.

Oxide hydrates and active oxides. XLIX. System lanthanum trioxide–water. G. F. Hüttig and M. Kantor (Z. anorg. Chem., 1931, **202**, 421—428; cf. A., 1931, 1235).—Isobaric dehydration curves for a number of specimens of hydrated La_2O_3 and *X*-ray diagrams indicate the existence of a stable cryst. $La_2O_3,3H_2O$, which is converted on dehydration into amorphous La_2O_3,H_2O. 0·5 mol. H_2O is still retained after heating at 700°. The dehydration curve closely resembles that of hydrargillite. F. L. Usher.

Polytherms of ternary systems containing water, alkali sulphate, and a sulphate of the vitriol type. IV. A. Benrath (Z. anorg. Chem., 1931, **202**, 161—171).—The solubilities of $ZnSO_4,H_2O$ and $CoSO_4$ have been redetermined. The transition temp. $ZnSO_4,6H_2O \rightleftharpoons ZnSO_4,H_2O$ is 55·5° (lit. 70°). $CoSO_4,H_2O$ is formed only very slowly, the transition temp. being about 71°. Isotherms (0—100°) for the systems $ZnSO_4$–$(NH_4)_2SO_4$–H_2O, $ZnSO_4$–Tl_2SO_4–H_2O, $MgSO_4$–Tl_2SO_4–H_2O, $CoSO_4$–Na_2SO_4–H_2O, and $NiSO_4$–Na_2SO_4–H_2O have been determined. The only double salts observed are $ZnSO_4,(NH_4)_2SO_4.6H_2O$, $ZnSO_4,Tl_2SO_4,6H_2O$, $MgSO_4,Tl_2SO_4,6H_2O$, $CoSO_4,Na_2SO_4,4H_2O$, and $NiSO_4,Na_2SO_4,4H_2O$. Of these, only the first-named dissolves congruently throughout the whole temp. interval. H. F. Gillbe.

Systems strontium oxide–arsenic pentoxide–water and lead oxide–arsenic pentoxide–water at 25° (acid range), and a basic strontium arsenate. H. V. Tartar, M. R. Rice, and B. J. Sweo (J. Amer. Chem. Soc., 1931, **53**, 3949—3956).—Equilibrium diagrams for the two systems defining the existence at 25° of the two acid Sr arsenates and the two acid Pb arsenates are given. The prep. of a *basic Sr arsenate*, $[Sr_3(AsO_4)_2]_3,Sr(OH)_2$, is described. M. G. Moore (*c*).

Formation of barium silicates from barium carbonate and silicic acid in the solid state. G. Grube and R. Trucksess (Z. anorg. Chem., 1931, **203**, 75—96).—The equilibrium pressure of CO_2 in each stage of reaction between $BaCO_3$ and SiO_2 has been measured. Four stages are recognised and their approx. heats of reaction have been determined as follows: $BaO+SiO_2=BaO,SiO_2+26$ kg.-cal.; $BaO,SiO_2+BaO=2BaO,SiO_2+21$ kg.-cal.; $2BaO,SiO_2+BaO=3BaO,SiO_2+13$ kg.-cal.; $3BaO,SiO_2+BaO=4BaO,SiO_2+4$ kg.-cal. E. S. Hedges.

Desulphurisation of steel. G. Tammann and H. O. von Samson-Himmelstjerna (Z. anorg. Chem., 1931, **202**, 329—336).—The occurrence or non-occurrence of a reaction between FeS and various oxides and carbonates has been deduced from the form of the heating curves obtained by heating FeS with each of the substances examined. Positive effects were obtained with CaO, BaO, and PbO. When Fe containing FeS is heated at 1700° with Pb, a part of the S is removed as PbS, but no desulphurisation occurs when the content of S is below 0·014%. F. L. Usher.

Equilibria between metals and slags in melts. I. Equilibrium $FeO+Mn \rightleftharpoons Fe+MnO$ at 1550—1560°. W. Krings and H. Schackmann (Z. anorg. Chem., 1931, **202**, 99—112).—The equilibrium const. $k=[Mn].(FeO)/[Fe].(MnO)$, where [Fe] and [Mn] are concns. in the metal phase and (FeO) and (MnO) those in the slag phase, is $0·0032\pm0·0005$ at 1550—1560°. The mass-action and Nernst partition laws are valid. The results are discussed in relation to the influence of impurities and the dissociation of silicate in the melts. H. F. Gillbe.

Phase boundary surfaces, phase boundary lines, and phase boundary points. W. Ostwald (Z. physikal. Chem., 1931, **158**, 91—96).—The theoretically possible types are enumerated, and other types of boundary strata are pointed out. R. Cuthill.

Third law of thermodynamics. W. H. Rodebush (Physical Rev., 1930, [ii], **35**, 210).—A discussion. L. S. Theobald.

Energy diagrams of the hydrogen halides in the gaseous state and in aqueous solution. P. J. Van Rysselberghe (J. Physical Chem., 1931, **35**, 3371—3378).—By combining data for heats of dissociation, ionisation, solvation, and dissolution, the energy of mutual polarisation of H and halogen atoms is calc. to be about 1 volt-electron. F. D. Rossini (*c*).

Methods and apparatus in use at the Bureau of Physico-Chemical Standards. V, VI. Heats of combustion. M. Beckers (Bull. Soc. chim. Belg., 1931, **40**, 518—570).—Apparatus and technique for the precise measurement of heats of combustion are described. The measured heat of combustion of salicylic acid is 5237·2 g.-cal., and in consideration of the results of other investigators, the standard val. recommended is 5237·5 g.-cal. (15°) per g. of acid weighed in vac. The greatest deviation from this val. is 0·015%. Salicylic acid is recommended as a second standard provided that the technique is such as to ensure complete combustion (in respect of which it is less satisfactory than BzOH). The objection that salicylic acid also exists in an unstable form is refuted by showing that if an unstable modification exists (which is doubtful) it is converted into the stable form by pressure in making the pastille. E. S. Hedges.

Heat of absorption of hydrogen by palladium-black at 0°. L. J. Gillespie and H. A. Ambrose (J. Physical Chem., 1931, **35**, 3105—3110).—The internal energy increase in the reaction $H_2+4Pd=2Pd_2H$ is -8740 g.-cal.$_{15}$, which gives -9280 g.-cal.$_{15}$ for the increase in heat content. These vals. agree with the vals. from v.-p. data. The average composition of the two solid phases formed corresponds with the formula Pd_2H. F. D. Rossini (*c*).

Free energies of formation and heats of formation of thallium amalgams. C. E. Teeter, jun. (J. Amer. Chem. Soc., 1931, **53**, 3917—3927).—Mol. free energies of formation at 20° and 40° have been calc. from published e.m.f. data. The heats of formation at 20° and 30° are positive. L. P. Hall (*c*).

Heats of dissolution, heats of formation, and free energies of formation of cadmium amalgams. C. E. Teeter, jun. (J. Amer. Chem. Soc., 1931, **53**, 3927—3940; cf. A., 1928, 710).—The heats of dissolution in Hg of Cd-rich amalgams at 25° have a max. negative val. at 22·5% Cd, representing a physical transition point and not a compound, since at 30° the max. is shifted to 24% Cd. Mol. heats of formation calc. from these thermal data do not agree with those calc. from e.m.f. temp. coeffs. Mol. free energies at 25° have been calc. from the recorded e.m.f. L. P. Hall (*c*).

Hydrazine. Mobility of hydrazinium ion at 25°. E. C. Gilbert (J. Amer. Chem. Soc., 1931, **53**, 3956—3962).—The conductivities at 25° of several N_2H_4 salts have been determined. At low concn. the slope of the curve obtained by plotting Λ against $\sqrt{C}$ is quite close to that calc. from the Onsager equation (A., 1927, 517). The mobility of the hydrazinium ion at 25° is 58·6—59·1.

W. C. Fernelius (*c*).

Dispersion of the electrical conductivity of some aqueous and non-aqueous electrolyte solutions. H. Gaertner (Physikal. Z., 1931, **32**, 919—926).—Variation of conductivity with the frequency of applied potential was determined for aq. solutions of $CaCrO_4$, $MgCrO_4$, $Ca_2Fe(CN)_6$, and for solutions of $MgSO_4$ in glycerol and MeOH; addition of 4% of H_2O to glycerol gave a large change in the time of relaxation. A. B. D. Cassie.

Electromotive force of cell $Zn(s)|ZnSO_4(m)|PbSO_4(s)|Pb(s)$. Experimental determination of the temperature coefficient of the ion size parameter in the theory of Debye and Hückel. I. A. Cowperthwaite and V. K. La Mer (J. Amer. Chem. Soc., 1931, **53**, 4333—4348).—E.m.f. measurements have been made at concns. of 0·0003—0·01*M* and at 0—50°, the results being compared with those predicted by the first approx. equation of the Debye-Hückel theory and by the Gronwall, La Mer, and Sandved extension. The simple Debye theory requires negative ionic sizes, which change rapidly with temp. and concn., whilst the parameter *a* of the extended theory remains const. at 3·64 Å.

M. Dole (*c*).

Theory of glass electrode. M. Dole (J. Amer. Chem. Soc., 1931, **53**, 4260—4280).—The H electrode function of thin glass films is attributed to their selective permeability towards $H^{\cdot}$ or the mobility of $H^{\cdot}$ across the interface glass–aq. solution. The deviations of the glass electrode potentials from the theoretical H electrode potentials in alkaline solution are attributed to an appreciable mobility of $Li^{\cdot}$, $Na^{\cdot}$, and $K^{\cdot}$ across the interface. Quant. agreement with this theory is obtained on application of the Henderson liquid-junction equation up to p_H 12 if it is also assumed that the $H^{\cdot}$ mobility increases relatively to that of $Li^{\cdot}$, $Na^{\cdot}$, or $K^{\cdot}$ as the p_H rises. The mobility through the interface may depend on the nature of the Helmholtz double layer. The experimental results agree with the equation $\log(e^{F\Delta E/RT}-1)=A+np_H$, where *A* and *n* are consts. and ΔE is the deviation of the glass electrode potential from its theoretical val.

M. Dole (*c*).

Acid standard cells of the unsaturated type. Y. Ishibashi and T. Ishizaki (Rev. Sci. Instr., 1931, [ii], **2**, 785—796).—The solubility of $CdSO_4$ in dil. H_2SO_4, and the connexion between e.m.f. and concn. of $CdSO_4$ and H_2SO_4 have been determined. Acid unsaturated cells are reproducible to 0·00003 volt. Hysteresis is small. A cell with an electrolyte containing 43·0% $CdSO_4$ and 0·05*N*-acid gives an e.m.f. of 1·08840 volt at 20°, and has practically no temp. coeff.

C. W. Gibby.

Correlation between rate of oxidation and potential in iron systems. L. Michaelis and C. V. Smythe (J. Biol. Chem., 1931, **94**, 329—340).—Comparison of the normal oxidation–reduction potentials at const. p_H of a series of salts and cyanide complexes of Fe referred to the H electrode shows that the autoxidisability of the $Fe^{\cdot\cdot}$ compound increases as the potential becomes more negative. Davidson's val. of 0·491 volt for $Na_3[Fe(CN)_5,H_2O]$ (A., 1928, 1330) places this compound in an anomalous position in the series; reinvestigation yields a lower val. compatible with its relative autoxidisability.

A. Cohen.

Discontinuous variation in e.m.f. of photo-electric cells containing a coloured liquid. A. Grumbach and F. Taboury (Compt. rend., 1931, **193**, 1178—1180).—With a cell similar to that described previously (cf. A., 1929, 1393), the electrolyte containing 0·052 g. of acid fluorescein and 6 mols. of H_2SO_4 per litre, and a new method of measurement, the results are irregular, save that there is a marked tendency for the e.m.f. to assume one or other of a series of vals. given by $V=nV_1$, *n* being a whole no., and $V_1=1\cdot3\times10^{-3}$ volt. An electrolyte containing 0·018 g. of fluoran and 8·4 mols. of H_2SO_4 per litre gives similar results. C. A. Silberrad.

Law of equidistance in photo-electric cells. A. Grumbach and F. Taboury (Compt. rend., 1932, **194**, 84–86; cf. preceding abstract).—Capillary and quadrant electrometers give similar results with H_2O and with solutions of acid fluorescein and Congo-red. This similarity obtains whether the cell is illuminated or not. The effect is attributed to alternate formation and removal of adsorbed unimol. layers by the electrode. C. A. Silberrad.

Influence of electrolytes on photo-electric phenomena. R. Audubert (Compt. rend., 1932, **194**, 82—84).—Using electrodes of CuI, Cu_2O, CuO,

Ag_2S, AgI, and Hg_2I_2, the influence on the photo-electric effect of aq. K_2SO_4 buffered by mixtures of citric acid and Na_2HPO_4 of p_H 9—2·8 shows that positive photo-potential is raised and negative lowered by a diminution in p_H, and conversely. The effects for 24 other salts of various metals show that the negative potential of an electrode exhibiting such in aq. K_2SO_4 is increased in an oxidising and diminished in a reducing solution; in all cases the effect is diminished by increased concn. of cations. The results support the author's theory (cf. A., 1931, 999). C. A. SILBERRAD.

Limits of gaseous explosions. M. NEUMANN and A. SERBINOFF (Nature, 1931, 128, 1040—1041).—For a certain range of temp. 3 pressure limits of ignition exist for a stoicheiometric mixture of CH_4 and O_2. Details are given for such a mixture in a cylindrical quartz vessel 3 cm. in diameter. L. S. THEOBALD.

Flame temperatures of mixtures of air with methane and oxygen, with methane and hydrogen, and with methane and acetylene. G. W. JONES, B. LEWIS, and H. SEAMAN (J. Amer. Chem. Soc., 1931, 53, 3992—4001; cf. A., 1931, 572).—Flame temp. for mixtures in various proportions have been determined, the max. temp. in each case being reached with a mixture slightly on the rich side. The max. flame temp. of any mixture of CH_4 and H_2 with CH_4 and C_2H_2 can be calc. by the additive principle from the max. flame temp. of the constituent mixtures. R. H. CHERRY (c).

Rate of formation of bromine chloride from its elements in the gas phase. W. JOST (Z. physikal. Chem., 1931, B, 14, 413—420).—At room temp. the reaction is bimol. and homogeneous, with a heat of activation of about 14 kg.-cal. R. CUTHILL.

System iodine–excess of sodium hydroxide. E. CARRIÈRE and JUILLARD (Compt. rend., 1931, 193, 1426—1428).—The formation of IO′ is accelerated by increase of alkali and by rise of temp., whilst the transformation into IO_3' is little affected by either. At 50° the formation of IO′ is practically instantaneous. The results agree with those of Schwicker (cf. A., 1895, ii, 213). C. A. SILBERRAD.

Saponification of di-esters M. RITCHIE (J.C.S., 1931, 3112—3125).—Vals. are reported of k_1 and k_2, the first and second stage velocity coeffs., for Et succinate, malonate, and substituted malonates in H_2O and H_2O–EtOH mixtures at 0°, 15°, and 25°. Two general ways of calculating k_1 from the data are developed; k_2 was calc. from measurements on the mono-ester by the classical bimol. equation. Increasing EtOH content reduces k_1 and k_2, which tend to zero for pure EtOH, and also reduces k_1/k_2. C. W. DAVIES.

Kinetic salt effect in methyl alcohol solutions. Reaction between sodium bromoacetate and sodium methoxide. A. N. KAPPANNA and H. W. PATWARDHAN (J. Indian Chem. Soc., 1931, 8, 541—548).—The rate of reaction of $CH_2Br{\cdot}CO_2Na$ with NaOMe in MeOH solution at 50° and 60° increases with increasing ionic concn. in accordance with Brönsted's theory, but the results do not agree even approx. with the Debye–Hückel theory. The temp. coeff. of the bimol. velocity coeff. is independent of the ionic concn., but has a much higher val. (3·273) than is usual for aq. solutions. The reaction velocity is increased by adding NaBr. E. S. HEDGES.

Kinetics of the inversion process in dilute solutions of sucrose in presence of hydrochloric acid. A. N. KAPPANNA and J. G. SHRIKHANDE (J. Indian Chem. Soc., 1931, 8, 557—569).—The inversion of sucrose in dil. solution at 35° and 45° has been followed by chemical analysis. At const. concn. of HCl (0·1N) the velocity coeff. increases with the concn. of sucrose (0·002924M—0·2924M), but not so greatly as the rate of increase of $a_{H^{\cdot}}$. The temp. coeff. is 3·505, independently of the concn. When the concn. of sucrose is const. at 0·02924M, the velocity coeff. is proportional to the concn. of HCl up to 0·01N and then increases at a greater rate. The velocity coeff., V, up to 0·12N-HCl is expressed by $0{\cdot}434V=1{\cdot}376\times10^{-2}+0{\cdot}84\times10^{-2}C$, where C is the concn. of HCl. The effect of KCl, NaCl, and LiCl (0·10—3·0N) on the velocity coeffs. is expressed by $k=k_0e^{ac}$, where a, the characteristic const., is 0·135 for KCl, 0·1564 for NaCl, and 0·1767 for LiCl. The increase in $a_{H^{\cdot}}$ does not account for the effect of the neutral salts. E. S. HEDGES.

Significance of velocity measurements in relation to the benzene substitution problem. D. H. PEACOCK (Nature, 1932, 129, 57).—Mainly a discussion. In the reaction between *o*-, *m*-, or *p*-toluidine and CH_2PhCl the energy of activation of the *o*- is higher than that for the *p*-compound. L. S. THEOBALD.

Origin of explosive wave in mercury fulminate. M. PATRY and P. LAFFITTE (Compt. rend., 1931, 193, 1339—1342).—By using trains of fulminate of definite rectangular cross-section and ignited as before (cf. A., 1931, 1020) it is found that the distance from the point of ignition at which an explosive wave is formed is, for the same cross-section, greater as the height is less, that no such wave is formed if the cross-section is less than 30 sq. mm., and that the velocity of the wave increases with, but not proportionally to, the cross-section. C. A. SILBERRAD.

Dilution theory of detonation. I. A. J. DUFF (J. Inst. Petrol. Tech., 1931, 17, 697—737).—A mathematical study of the auto-ignition theory of "pinking." N. H. HARTSHORNE.

Behaviour of atomic hydrogen. III. Mercury hydride. A. KLEMENC and F. PATAT (Z. physikal. Chem., 1931, 158, 65—77).—The vals. for the v. p. of Hg at 7—10° obtained by the gas-saturation method when H_2 under a pressure of 1 atm. or a mixture of H_2 and N_2 in which the partial pressure of the H_2 is 1—2 mm. is used as the inert gas and the evaporating Hg is irradiated with the light from a Hg-vapour lamp are the same as those obtained with pure N_2 without irradiation. It is concluded that the velocity coeff. of the unimol. decomp. of HgH must be of the order of 10^{11} mols. per c.c. per sec., and that the reactions in the system Hg–H_2 under the influence of the resonance line 2536 Å. are brought about by at. H, not by HgH. R. CUTHILL.

Reactions in the solid state at high temperatures. IX. Variation of the reaction velocity with the relative proportions and method of preparation of the components and with the presence of admixtures. W. Jander and E. Hoffmann (Z. anorg. Chem., 1931, **202**, 135—153).—The velocities of the reaction between $BaCO_3$ and SiO_2 and between $CaCO_3$ and MoO_3 have been studied under varying conditions of origin and purity of the reactants and in presence of 5% of TiO_2 or CaF_2, or of WO_3 or NaCl, respectively. Variation of the method of prep. of the reactants is without influence on the amount of energy, *q*, necessary to produce migration of the atoms in the lattice, although it alters the number of points at which diffusion takes place; the presence of admixtures produces small variations of *q* and considerable change of the number of active centres. *q* is dependent on the relative proportions of the reactants only if more than one compound is formed in the system. H. F. Gillbe.

Passivity of iron. U. R. Evans (Nature, 1931, **128**, 1062—1065).—A summary.
L. S. Theobald.

Influence of metallic impurities on the rate of dissolution of base metals. G. Tammann and F. Neubert (Z. anorg. Chem., 1931, **201**, 225—244).—The rate of evolution of H_2 from dil. acids by Zn, Fe, or Al can be expressed by $v=at+bt^2$, where v is the vol. liberated at time t. The const. a is characteristic of the base metal and is not affected by impurities, whereas b represents the accelerating influence of local galvanic elements, and usually increases with increasing concn. of a nobler metal, with the exception of Si or Sn in Al. The rate of dissolution of Fe–C alloys is almost const. until the pearlite concn. is exceeded, when the rate increases rapidly with C content. Zn and Fe dissolve in $(NH_4)_2S_2O_8$ at a const. rate which is but little affected by foreign metals. F. L. Usher.

Attack of platinum and tungsten by iodine. G. van Praagh and E. K. Rideal (Proc. Roy. Soc., 1931, A, **134**, 385—404).—The metals were in the form of wire, the Pt being 0·007 cm. and the W 0·005 cm. in diameter. With Pt no surface attack occurs at relatively low temp., but dissociation of mol. I takes place at about 1300° abs. At. I attacks Pt at 1400°, forming volatile PtI and PtI_2. The abs. rates of the reactions are discussed and the heat of adsorption of at. I in Pt is calc. to be 53,700 g.-cal. per mol. The emissivity of Pt is unaltered by the action of I up to 1700° abs.; therefore this method cannot detect the unimol. adsorbed layer of the complex PtI formed at all temp. below 1560° abs. The difference between the metals was anticipated from the difference between their work functions. At low temp. W is attacked by I, but at high temp. dissociation of I occurs more readily on the Pt.
L. L. Bircumshaw.

Topochemistry of corrosion and passivity. II. Investigation of initial step in corrosion of soft iron. E. Pietsch, B. Grosse-Eggebrecht, and W. Roman (Z. physikal. Chem., 1931, **157**, 363—388; cf. A., 1931, 1374).—A homogeneous surface of soft Fe brought in contact with aq. H_2O_2 at room temp. becomes passive, and neither rusts nor decomposes the H_2O_2. Addition of AcOH or barbituric acid has no effect, but rusting starts some time after addition of HCl. When the passive Fe is immersed in boiled-out H_2O rust appears, after a period of induction, at the grain boundaries, and spreads autocatalytically over the grain surfaces. The wt. of Fe dissolved from a homogeneous surface by dil. H_2SO_4 is a linear function of the length of grain boundary in the surface. It is therefore concluded that the initial step in corrosion is the adsorption of the corroding medium at grain boundaries or other active linear discontinuities, such as the boundary between the Fe and an indifferent substance of high surface tension, *e.g.*, paraffin wax. It is suggested that in rusting the H_2O is adsorbed and the OH is drawn into a closer resonance union with the Fe than with the H, which leads to the formation of $Fe(OH)_2$. In presence of H_2O_2 the active centres are blocked by adsorbed O, formed by a minute decomp. of H_2O_2, the adsorption of H_2O thus being prevented. An Fe surface which is not homogeneous, *i.e.*, has been insufficiently polished, or contains cavities, is attacked by H_2O_2 at once, presumably because it possesses centres sufficiently active to adsorb H_2O as well as O. R. Cuthill.

Reactions between gas and solid. I. Velocity of absorption of moisture by quicklime. T. Aono (Bull. Chem. Soc. Japan, 1931, 6, 294—301).—The velocity of absorption of H_2O from damp air by CaO has been studied under various conditions of humidity and temp. The first product of the reaction is $Ca(OH)_2$, which then adsorbs more H_2O.
D. R. Duncan.

Decomposition of hydrogen peroxide by traces of metallic salts. H. Tatu (Tiba, 1931, 9, 473—477).—Ca salts had practically no effect. In neutral solution the decomp. after 21 days with additions of 0·05 or 0·10 g. per litre (2·5% H_2O_2), respectively, of metals was: Cu 72·4, 76·4; Mn 43·2, 49·6; Fe 50·4, 66·4%. In acid solution it was: Cu 38·4, Mn 22, Fe 81·2%. In alkaline solution decomp. in presence of Mn is practically complete in 20 min.
Chemical Abstracts.

Interaction between copper oxide and neutral salt solutions. M. P. V. Iyer (J. Indian Chem. Soc., 1931, 8, 613—618).—When CuO is shaken with neutral salt solutions, OH′ is adsorbed primarily and the complex reacts with the neutral salt with the liberation of alkali. The total amount of alkali liberated is $1·3904\times10^{-6}$ g.-ion per g. of CuO. The nature of the cation has little influence on the amount of alkali liberated, but the valency of the anion is important and follows the series $SO_4'' > Cl' > NO_3'$. The liberation of alkali is closely connected with the electrokinetic behaviour of CuO in contact with different electrolytes. E. S. Hedges.

Catalytic effect of ferricyanide in the oxidation of unsaturated compounds by oxygen. G. P. Wright, J. B. Conant, and S. E. Kamerling (J. Biol. Chem., 1931, **94**, 411—413).—In Na_2CO_3 solution oleic acid is not oxidised by ferricyanide in the absence of O_2, neither is ferrocyanide oxidised by O_2 in the same medium. The catalytic oxidation of oleic acid (A., 1931, 758) is therefore not a cyclic process, in which the latter reduces ferricyanide, and the ferrocyanide produced is re-oxidised. The oxidation may be a chain reaction initiated by ferricyanide.

A. Cohen.

Constitutional factors controlling prototropic changes in carbonyl compounds. I. Relative speeds of enolisation of acetone and bromoacetone and the effect of the acid catalyst. E. D. Hughes, H. B. Watson, and E. D. Yates (J.C.S., 1931, 3318—3324).—The mechanism of bromination is the same for bromoacetone and $COMe_2$, so velocity measurements give the speed of enolisation. This is greater for the Br-compound in absence of catalyst, but is far less accelerated by acid. On the assumption that enolisation involves (*a*) ionisation of an α-H atom and (*b*) co-ordination of the CO-oxygen with H_2O or $H_3O^{\cdot}$, the two effects are explained by electron drift; the Br favours process (*a*), but hinders the co-ordination with a positive group.

C. W. Davies.

So-called autoxidation of cysteine. C. A. Elvehjem (Science, 1931, 74, 568—569).—A criticism (cf. A., 1931, 1246). The so-called autoxidation of cysteine may be due to the presence of Cu.

L. S. Theobald.

Reaction of active nitrogen with hydrogen atoms at metal surfaces. J. K. Dixon and W. Steiner (Z. physikal. Chem., 1931, **B**, 14, 397—406; cf. A., 1930, 1378).—The formation of NH_3 from active H and N is greatly accelerated by an Fe, Ni, or Cu surface, whereas the rate of formation of N_2H_4 is considerably reduced. The most satisfactory explanation of the reaction is that some of the adsorbed H atoms recombine, but others react with N atoms impinging on the surface from outside, $N+H=NH$. The NH mols. then undergo the reactions $NH+H_2=NH_3$, $NH+NH=N_2+H_2$, $NH+H=N+H_2$, $NH+N=H+N_2$, $NH+H=NH_2$, of which the first is the most probable, and the NH_2 formed in the last reacts as follows: $NH_2+NH_2=N_2H_4$, $NH_2+H=NH_3$. The yield of NH_3 is independent of the area of catalyst surface. R. Cuthill.

Oxide hydrates and active oxides. XLVII. Active states of metallic oxides. E. Rosenkranz (Z. physikal. Chem., 1931, **B**, 14, 407—412; cf. A., 1931, 1235).—The activity in catalysing the decomp. of MeOH and of aq. $AgNO_3$ of ZnC_2O_4 which has been partly converted into ZnO by heating is not a linear function of the ZnO content, but may pass through a max. and fall again as the proportion of ZnO increases. These observations are taken to mean that the ZnO formed directly from the ZnC_2O_4 is unstable, and passes through a series of states of differing activity before reaching the final stable state. R. Cuthill.

Blanc's alumina. N. Parravano (Mem. R. Accad. Ital., 1930, **1**; Chem. Zentr., 1931, i, 2521; cf. A., 1930, 437).—Al_2O_3 obtained by prolonged heating of $AlCl_3,6H_2O$ at 350—450° (Blanc's alumina) is a good catalyst for converting EtOH into Et_2O. EtOH is unchanged, however, when Al_2O_3 in which the at. distances have been reduced by heating is used.

L. S. Theobald.

Catalytic oxidation of sulphur dioxide in the presence of tin vanadate. E. B. Maxted and N. J. Hassid.—See B., 1932, 20.

[Catalytic] preparation of acetic acid from methyl alcohol and carbon monoxide. E. A. Shilov.—See B., 1932, 12.

[Catalytic] synthesis of methyl alcohol from carbon monoxide and hydrogen under pressure. V. A. Plotnikov and K. N. Ivanov.—See B., 1932, 11.

Oxidation of ethyl alcohol by air in presence of carbon–copper catalysts. Martineau (Compt. rend., 1931, 193, 1189—1192).—A catalyst prepared by action of aq. NH_3 on an intimate mixture of C with Cu hydroxide or carbonate, drying at 140°, and heating at 250° in a covered vessel to liberate Cu, brings about oxidation of EtOH to MeCHO by air at 63°, the max. catalytic activity being observed with a ratio Cu : C of 1 : 2—3 according to the temp. Activated C or Cu alone or in admixture does not bring about the oxidation below 110°.

H. A. Piggott.

Catalytic oxidation of ethyl alcohol. A. R. Day (J. Physical Chem., 1931, 35, 3272—3279; cf. A., 1930, 1381).—In the vapour-phase oxidation of EtOH with a Ag catalyst the presence of a small quantity of Sm_2O_3 in the catalyst slightly increases the yield of MeCHO at a low catalyst temp. Higher yields were obtained in a one-step oxidation than have previously been attained by similar methods. The yield was 79·5% with a catalyst at 370° containing 2·7858 g. Ag and 0·0075 g. Sm_2O_3.

F. L. Browne (*c*).

Vapour-phase esterification in presence of silica gel. H. C. Tidwell and E. E. Reid (J. Amer. Chem. Soc., 1931, **53**, 4353—4358; cf. A., 1924, ii, 667).—The esterification of EtOH and AcOH has been studied at 150—300°. The limiting conversion obtained with an equimol. mixture of alcohol and acid was approached from the other side of the equilibrium point by the hydrolysis of an acetate–H_2O mixture, the average conversion being about 85% at 150° and 75% at 300°. These data indicate that the equilibrium const. varies somewhat with temp.

C. J. West (*c*).

Beryllium. III. Electrolysis of solutions of beryllium compounds in liquid ammonia. H. S. Booth and G. G. Torrey (J. Physical Chem., 1931, 35, 3111—3120; cf. A., 1931, 1249).—Be obtained by electrolysis of solutions of $BeCl_2$ or $Be(NO_3)_2$ in liquid NH_3 is so pure that it can be dissolved in ordinary reagents only with difficulty. The decomp. voltage of the $BeCl_2$ solution is approx. 3·5 volts.

I. J. Patton (*c*).

Electrodeposition of metals from anhydrous ammonia. H. S. Booth and M. Menahem (J. Physical Chem., 1931, 35, 3303—3321).—Cu, Ag, Au, Be, Zn, Cd, Hg, Tl, Sn, Pb, As, Cr, Mn, Fe, Ni, Co, Pd, and Pt can be successfully deposited from anhyd. NH_3 solutions at the b. p. Al, Th, Bi, Sb, Mo, and W do not deposit either at the b. p. or at room temp. under pressure. A cell for high-pressure electrodeposition is described. R. H. Cherry (*c*).

Electrodeposition of iron, copper, and nickel alloys from cyanide solution. I. L. E. Stout and C. L. Faust.—See B., 1932, 66.

Effect of mercury in zinc cyanide plating solutions. M. de K. Thompson and W. E. Charles. —See B., 1932, 66.

Stability of cadmium cyanide plating solutions. S. Wernick.—See B., 1932, 67.

Reaction at the quinhydrone electrode in methyl alcohol. A. Macfarlane (J.C.S., 1931, 3212—3218).—The rate of fall in potential of the quinhydrone electrode in MeOH solutions of HCl is explained by a slow oxidation of the HCl to Cl_2 by dissolved O_2. This is followed by substitution: $Cl_2+Q\longrightarrow HCl+QCl$, and $QCl+HQ\rightleftharpoons HQCl+Q$, where Q and HQ are respectively benzoquinone and quinol. C. W. Davies.

Reactions in the brush discharge. A. P. Davis (J. Physical Chem., 1931, 35, 3330—3352).— $COMe_2$ is entirely converted into gaseous products, the principal reaction being $COMe_2=C_2H_6+CO$; H_2, C_2H_4, and C_2H_2 are formed by decomp. of the C_2H_6. The $COMe_2$ undergoes little condensation, but yields keten by pyrolysis. From C_6H_6, which forms gas much more slowly than $COMe_2$, there are obtained a resinous substance, $(C_6H_4)_n$, and Ph_2, without, however, the H eliminated in the formation of these compounds appearing as such in the products of reaction. R. H. Cherry (*c*).

Chemical action in the glow discharge. VIII. Effect of cathode material. P. D. Kueck and A. K. Brewer (J. Physical Chem., 1931, 35, 3207—3213; cf. A., 1931, 919).—The rate of synthesis of H_2O and of NH_3 in the negative glow is in general directly proportional to the normal cathode falls of potential for the various metals used as cathodes, which is attributed to an increase in positive ion production with increased electron acceleration. The anode material has no effect on the rate of reaction. P. H. Emmett (*c*).

Chemical action of the electric discharge. V. Influence of the nature of the electrodes on the production of nitric oxide in the electric arc. E. Briner, J. Corbaz, and C. Wakker (Helv. Chim. Acta, 1931, 14, 1307—1314).—By coating the platinum electrodes with paraffin mixed with $BaCO_3$ or $CaCO_3$, and heating, adherent oxide deposits are obtained and the yield of NO (per kv.-amp.-hr.) is increased by 20—40%. Ni electrodes could not be similarly covered. With a Li phosphate deposit the increase of yield is up to 71%. The yields obtained with Cu and Ag electrodes are increased by 50—70% if the electrodes are alloyed with Li or Ca (0·8—4%). H. F. Gillbe.

Photochemical kinetics of hydrogen–chlorine reaction. Formation of hydrogen chloride on absorption of light in the banded region of the chlorine spectrum. E. Hertel (Z. physikal. Chem., 1931, **B**, **14**, 443—456).—The reaction velocity is given by $dx/dt=k[H_2][Cl_2]\{n[H_2]+p[Cl_2]+q[HCl]\}$, where $n=1$, $p=3$, and $q=0{\cdot}5$, which becomes $dx/dt=k_1[H_2][Cl_2]^2$ when there is a great excess of Cl_2, and $dx/dt=k_2[H_2]^2[Cl_2]$ when the H_2 is present in great excess. The yield per quantum is of the order of 10^4—10^5. O_2 retards the reaction, the velocity equation becoming $dx/dt=\{k[Cl_2]^2/[O_2]\}\{n[H_2]+p[Cl_2]+q[HCl]\}$. The general velocity equation may be deduced by assuming that the primary reaction is the formation of excited Cl_2 mols. by absorption of light. A small fraction of these is dissociated by impact with H_2, Cl_2, and HCl mols., the efficiencies of which in effecting dissociation are in the ratio 1 : 3 : 0·5. The Cl atoms then react as follows: $Cl+H_2=HCl+H$, $H+Cl_2=HCl+Cl$. If O_2 terminates the reaction chains by combining with the H atoms, the observed velocity equation is accounted for. R. Cuthill.

Photochemical formation of ozone sensitised by zinc oxide. G. Jung and E. Kunau (Z. physikal. Chem., 1931, **B**, **15**, 45—50).—The photochemical formation of O_3 from O_2 in presence of ZnO (B., 1922, 392) occurs only when the ZnO has been prepared by ignition of $Zn(NO_3)_2$ and contains a little undecomposed nitrate. $Zn(NO_3)_2$ sensitises the reaction if hydrated, but not if anhyd. The sensitisation has no relation to the visible luminescence of ZnO. R. Cuthill.

Reaction $5As_2O_3\longrightarrow 3As_2O_5+4As$ as a pyrochemical and photochemical process. G. G. Reissaus (Z. angew. Chem., 1931, 44, 959—962).— The mechanism of the thermal conversion of arsenite into arsenate is invariably based on the reaction $5As_2O_3\longrightarrow 3As_2O_5+4As$, and does not involve direct oxidation by atm. O_2. In air, As_2O_3 is formed subsequently from the As liberated, and then undergoes further decomp.; the As thus acts as an O carrier. By heating As_2O_3 or an arsenite under pressure or in vac., pure As may be prepared. Commercial Pb arsenite, as well as specimens prepared by ordinary methods in the laboratory, are not photosensitive, but a dry mixture of PbO and As_2O_3 is remarkably sensitive, As being liberated in the reaction. It is probable that the salt as ordinarily prepared is $3Pb(OH)_2,As_2O_3$, since if it is prepared from As_2O_3 and PbO in the "nascent" state, *e.g.*, by heating $Pb(OH)_2$ with As_2O_3 and dil. NaOH solution, it is photosensitive. No other metallic arsenite has been found to be photosensitive. H. F. Gillbe.

Photographic emulsion; silver ion–gelatin equilibrium. B. H. Carroll and D. Hubbard (Bur. Stand. J. Res., 1931, 7, 811—825).—Measurements of the equilibrium between $Ag^{\cdot}$ and gelatin by means of a Ag electrode have shown a strong selective combination of $Ag^{\cdot}$ with gelatin. In the photographic emulsion, the gelatin may cause large changes in $[Ag^{\cdot}]$. No combination of gelatin with $Ag(NH_3)_2^{\cdot}$ was observed. Prolonged washing of AgBr– or AgCl–gelatin emulsions causes appreciable hydrolysis of the Ag halide, leaving an excess of Ag in combination with the gelatin. E. S. Hedges.

Chemical reactions induced by light. III. L. Vecchiotti and G. Zanetti (Gazzetta, 1931, 61, 798—802).—In a mixture of PhMe and $PhNO_2$ after exposure to sunlight for 5 months in a sealed tube NH_2Ph and azoxybenzene are found in addition to BzOH and *p*-aminophenol (A., 1930, 1180). The

mechanism of the reaction is explained. No reaction is caused by the sun's heat when light is excluded.
E. E. J. Marler.

Danger of explosion of alkali chlorates, especially sodium chlorate, from strong mechanical shocks. Lenze, Metz, and Rubens (Jahrb. Chem.-tech. Reichsanst., 1931, 8, 1—3; Chem. Zentr., 1931, i, 2446).—Pure $NaClO_3$ and $KClO_3$ are not exploded by intense blows or by rubbing. In contact, but not necessarily mixed, with inflammable org. matter explosions can be produced by such means.
L. S. Theobald.

Principles of genetic development of material. VI. Reactions within small bodies. Copper complexes. V. Kohlschütter [with H. Nitschmann] (Helv. Chim. Acta, 1931, **14**, 1215—1246).—The influence of temp. and concn. on the reaction between Cu and C_2O_4'' has been studied, together with the effect of the subsequent gradual addition of one of the reactants. The varieties of appearance and particle size of the ppts. are described. The pptn. is accelerated by H_2SO_4, without change of the cryst. form, but other additions cause a change of form. Some of the ppts. appear as somatoids, others as well-defined crystals, and others as amorphous powders, but the *X*-ray diagrams are all identical. The somatoids are probably developed from gel droplets, and the same may be true of the cryst. types, although the formation of these from the somatoids has not been observed. The production of the various forms is not a progressive process; each form is produced independently from the original materials. Formation of $Cu(OH)_2$ from the somatoids takes place without change of form, but the cryst. forms are destroyed during this process; somatoid $Cu(OH)_2$ may be reconverted into somatoids of CuC_2O_4. If the $Cu(OH)_2$ is treated with 10% H_2O_2, and the resulting CuO_2,H_2O reconverted into $Cu(OH)_2$, a much more reactive material is obtained, owing to destruction by the H_2O_2 of the central structure of the somatoid. Similar experiments have been made with $Cu(OH)_2$ derived from schönite and from basic nitrate and carbonate. The comparative catalytic activities of specimens of $Cu(OH)_2$ of different origins on the decomp. of H_2O_2 have been determined; the activity is governed, not merely by the particle size, but also by the internal structure of the particles; it is scarcely influenced by the nature of the envelope. The activity of the somatoids diminishes as the particles age, owing to structural changes, and is altered also by destruction of the internal orientation by mechanical means. The reaction involves the reversible formation of a Cu peroxide. The general nature of reactions within small particles, as opposed to reactions at the surface and in the bulk of the material, is discussed.
H. F. Gillbe.

Comparison of copper oxalate and polymethylene precipitates. H. W. Kohlschütter (Helv. Chim. Acta, 1931, **14**, 1246—1249).—A discussion of the preceding paper in relation to other published work (cf., *e.g.*, A., 1931, 198).
H. F. Gillbe.

Fluoroberyllates and their analogy with sulphates. I. N. N. Rây (Z. anorg. Chem., 1931, **201**, 289—300).—A close analogy of fluoroberyllates with sulphates is indicated by the physical properties of corresponding salts. Isomorphism of the Ba salts has been established by *X*-ray analysis. The following *compounds* are described: Li_2BeF_4,H_2O, d_4^{30} 1·944; Rb_2BeF_4, d_4^{30} 3·243; Cs_2BeF_4, d_4^{30} 4·213; Tl_2BeF_4, d_4^{30} 6·650; $BaBeF_4$, d_4^{30} 4·170; $PbBeF_4$, d_4^{30} 6·135; Ag_2BeF_4; $N_2H_6BeF_4$; $(NMe_4)_2BeF_4$; NMe_4HBeF_4.
F. L. Usher.

Azides of the alkaline-earth metals. Haid, Goetze, Selle, Koenen, Schmidt, and Becher (Jahrb. Chem.-tech. Reichsanst., 1931, 8, 102—108; Chem. Zentr., 1931, i, 2447).—An investigation of the explosibility of Ca, Ba, and Sr azides under different conditions shows that Ca azide is a much stronger explosive than those of Ba and Sr, which are approx. equal. Dry Ba azide can be transported in cardboard boxes in quantities up to 500 g., and with a H_2O content of 10% it is no longer a dangerous explosive.
L. S. Theobald.

Synthesis of β-calcium metasilicate (wollastonite) by a reaction between solids. H. Ehrenberg (Z. physikal. Chem., 1931, **B**, **14**, 421—434).—The formation of wollastonite on heating compressed pastilles of a mixture of calcspar and amorphous SiO_2 at 750—1000° has been demonstrated by *X*-ray examination.
R. Cuthill.

Hydrothermal synthesis of calcium silicates under ordinary pressure. II. S. Nagai (J. Soc. Chem. Ind. Japan, 1931, **34**, 418—422B; cf. B., 1932, 25).—Hydrothermal treatment of a $3CaO : 1SiO_2$ mixture for 1 hr. at temp. between 600° and 1100° gives $3CaO,2SiO_2$ and $2CaO,SiO_2$, the proportion of the latter increasing with rise of temp. to approx. 100% at 900°. A 1 : 2 mixture under these conditions gives CaO,SiO_2 and $3CaO,2SiO_2$, the proportion of the latter reaching 100% between 900° and 1000°, above which some $2CaO,SiO_2$ is formed. Treatment of a 1 : 1 mixture for 5 hr. at 900° and 1000° partly decomposes the $2CaO,SiO_2$ first formed into a less basic product, whilst under the same conditions 2 : 1 and 3 : 1 mixtures yield $2CaO,SiO_2$ almost exclusively.
N. H. Hartshorne.

Decomposition of tricalcium silicate in the temperature range 1000—1300°. E. T. Carlson (Bur. Stand. J. Res., 1931, 7, 893—902).—The decomp. of $3CaO,SiO_2$ into $2CaO,SiO_2$ and CaO, measured by determining the free CaO, is greatest at about 1175°; at 1300° it is almost negligible. The decomp. appears to be autocatalytic, the rate being increased by the presence of CaO or $2CaO,SiO_2$. Exposure to moist air promotes the decomp. Freshly-ignited $3CaO,SiO_2$, containing a min. amount of free CaO, decomposes very slowly. Gypsum accelerates the decomp., probably through the formation of CaO by dissociation.
E. S. Hedges.

Calcium chromo-, selenio-, and sulpho-aluminates. (Mlle.) Foret (Compt. rend., 1931, **193**, 1423—1425).—The double salts $3CaO,Al_2O_3,3CaA_2,30H_2O$, where $A=CrO_4$, SeO_4, or SO_4 (cf. A., 1915, ii, 50), are obtained by methods similar to those previously described (cf. A., 1930, 1386, 1537). On mixing clear solutions of calcium aluminate, CaA_2, and $Ca(OH)_2$ the cryst. double salt is pptd. $[CaO]$ should be $>3[Al_2O_3]$, $[CaA_2]\not<30[Al_2O_3]$, $[CaCrO_4]\not<0{\cdot}05M$, and $[CaSeO_4]\not<0{\cdot}32M$. The phase relations are discussed. C. A. SILBERRAD.

Double compound of aluminium chloride with hydrogen cyanide. L. E. HINKEL and R. T. DUNN (J.C.S., 1931, 3343).—HCN and finely-divided $AlCl_3$ give the *compound* $AlCl_3,2HCN$ as a white solid unstable in moist air and sol. in dry Et_2O.
C. W. DAVIES.

Double sulphates of metals of the rare earths and of the alkali metals. XIV. Sulphates of praseodymium and sodium. F. ZAMBONINI and S. RESTAINO (Atti R. Accad. Lincei, 1931, [vi], **14**, 69—71; cf. A., 1930, 1387).—The solubility isotherm at 25° shows that only two double sulphates are formed, $Pr_2(SO_4)_3,Na_2SO_4,2H_2O$ and $4Pr_2(SO_4)_3,5Na_2SO_4,8H_2O$. Some properties of these compounds are described. O. J. WALKER.

Thermal decomposition of the oxalates and nitrates of lanthanum, cerium, praseodymium, neodymium, and samarium in an atmosphere of carbon dioxide. T. SOMIYA and S. HIRANO (J. Soc. Chem. Ind. Japan, 1931, **34**, 459—461B).—Decomp. proceeds according to the schemes $M_2(C_2O_4)_3,nH_2O\longrightarrow M_2(C_2O_4)_3\longrightarrow[M_2(C_2O_3)_3]\longrightarrow[M_2O_3,2CO_2]\longrightarrow M_2O_3,CO_2\longrightarrow M_2O_3$, and $M(NO_3)_3\longrightarrow MO(NO_3)\longrightarrow M_2O_3,CO_2\longrightarrow M_2O_3$, where M is La, Pr, Nd, or Sm. The temp. of decomp. of M_2O_3,CO_2 rises with increasing basicity of M. $Ce_2(C_2O_4)_3,9H_2O$ and $Ce(NO_3)_3$ are converted into CaO_2.
N. H. HARTSHORNE.

Activation of carbon by means of carbon dioxide. P. P. KOSAKEVITSCH and M. A. ISMAILOV (Kolloid-Z., 1931, **57**, 294—302).—The activation of C by CO_2 is greatest after a certain duration of treatment, further treatment reducing the activity. The optimal duration is decreased by rising temp. and increasing velocity of the CO_2 stream. Differences in the behaviour of sugar- and wood-charcoals can be ascribed to the variation of ash content and porosity. Small quantities of Al_2O_3 accelerate the reaction between C and CO_2, but greater amounts have less influence, probably through forming a protective film. E. S. HEDGES.

Halogen compounds of non-metals. I. Silicon tetrabromide. II. Boron tribromide. E. POHLAND (Z. anorg. Chem., 1931, **201**, 265—281, 282—288).—I. $SiBr_4$ exists in a tetragonal modification, m. p. 2·4°, and a cubic, m. p. 5·2°. Density, refractive index, and heat of formation have been redetermined, and the chemical behaviour towards various compounds has been studied.

II. Physical consts. of BBr_3 have been redetermined and its chemical reactivity has been examined. *Compounds* BBr_3,HCN, m. p. 70°, and $BBr_3,AgCN$, indicating the co-ordination no. 4 for B, have been prepared. F. L. USHER.

Titanium nitride. S. UMEZU (Proc. Imp. Acad. Tokyo, 1931, 7, 353—356).—When fine-grained TiO_2 was heated with C in a slow stream of N_2 at different temp. for 1—4 hr., the % reduction to Ti_2O_3 reached a max. of about 43 at 1100°, above which it decreased and the % formation of TiN increased to about 90 at 1300°. These yields were lower when a coarser TiO_2 was used. TiO is much more readily converted into TiN by a stream of N_2 than is Ti_2O_3.
N. H. HARTSHORNE.

Action of ammonia and amines on germanium tetraiodide. T. KARANTASSIS and L. CAPATOS (Compt. rend., 1931, **193**, 1187—1189).—GeI_4 is prepared by dissolving GeO_2 in hot conc. aq. HI, and crystallising the evaporated product from $CHCl_3$. By passing NH_3 into, or adding liquid NH_2Et or a CCl_4 solution of the other amines to, a CCl_4 solution of GeI_4 the following *compounds* are obtained: $GeI_4,8NH_3$; $GeI_4,6NH_2Et$; $GeI_4,10NHEt_2$; $GeI_4,5NEt_3$; $GeI_4,4NH_2Ph$; $GeI_4,6(o\text{-})C_6H_4Me{\cdot}NH_2$; and $GeI_4,10C_9H_7N$. All are white cryst. powders except the quinoline compound, which is yellow.
C. A. SILBERRAD.

Preparation of lead disulphide by reaction between lead mercaptides and sulphur. W. E. DUNCAN and E. OTT (J. Amer. Chem. Soc., 1931, **53**, 3940—3949; cf. A., 1930, 1405).—*Lead disulphide*, PbS_2, a brown solid, is formed by the action of S on sec.-butyl Pb mercaptide in C_6H_6 solution, the ratio S : Pb being greater than 7. It decomposes into PbS and S at room temp., and with HCl yields H_2S_2.
M. G. MOORE (c).

Lead suboxide. P. PASCAL and P. MINNE (Compt. rend., 1931, **193**, 1303—1305).—That the product obtained by the decomp. of PbC_2O_4 in vac. at 275° (cf. A., 1917, ii, 141) is Pb_2O is confirmed by the fact that the magnetic susceptibility ($\times10^6$) thereof is $-0{\cdot}09$ as compared with $-0{\cdot}12$ and $-0{\cdot}19$, the susceptibilities of Pb and PbO, respectively. Reduction of PbO by $NHPh{\cdot}NH_2$ (cf. A., 1928, 721) yields a mixture of Pb and Pb_2O. C. A. SILBERRAD.

Mechanism of precipitation processes. VII. Thiocyanate compounds of lead. Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anorg. Chem., 1931, **202**, 62—72).—Pptn. of KCNS solution with a 10% excess of $Pb(OAc)_2$ solution yields, irrespective of concn. and temp., $Pb(OH)CNS$; in acid solution, or if the ratio $Pb(OAc)_2$: KCNS is less than 2, $Pb(CNS)_2$ is pptd. If $Pb(CNS)_2$ is boiled with NH_4OAc solution, $Pb(OAc)CNS$, and ultimately $Pb(OH)CNS$, are formed. The latter is stable at 50—60°, but is partly hydrolysed by H_2O at 100° and in sunlight it slowly decomposes into PbS. The solubility of $Pb(CNS)_2$ at 25° is 0·5347%, and is 25 times that of $Pb(OH)CNS$. The ppt. obtained with H_2SO_4 and $Pb(CNS)_2$ always contains CNS' (0·7—1·3%), but the quantity diminishes with time. Solutions of $Na_2C_2O_4$ and $Pb(CNS)_2$ yield almost pure PbC_2O_4, but the ppt. gradually absorbs a considerable quantity of CNS' from the solution; a compound $Pb(CNS)_2,PbC_2O_4$ is formed under certain conditions. H. F. GILLBE.

Formation of fluorophosphoric acid from phosphoric acid and aqueous hydrofluoric acid. W. LANGE and G. STEIN (Ber., 1931, **64**, [B], 2772—2783; cf. A., 1929, 764).—The equilibrium $H_3PO_4+HF\rightleftharpoons H_2PO_3F+H_2O$ has been investigated at 20° by withdrawal of aliquot portions of the mixture after definite intervals, neutralising, and cautiously adding dil. $AgNO_3$, whereby Ag_3PO_4 is exclusively

and quantitatively pptd. In H_2O the equilibrium is independent of the use of anhyd. or 90% H_3PO_4. Increasing amounts of H_2O initially decrease the formation of H_2PO_3F to an unusual extent, but below a certain concn. (initially about 60% H_3PO_4) further addition of H_2O has no unusual activity and appears to influence the equilibrium in accordance with the law of mass action. With increasing amounts of 41% HF there is initially increase in the amount of H_2PO_3F formed from anhyd. H_3PO_4. At a definite concn. the increase ceases abruptly and subsequently the amount of H_3PO_4 decreases slightly and then remains const. It appears that conc. H_3PO_4 contains a modification (? neutral, undissociated mols.) which reacts with HF according to an unknown law and passes when diluted with H_2O into other forms (? ions) of which at least one reacts with HF according to the law of mass action. With KH_2PO_4 and increasing amounts of 41% HF the PO_3F'' concn. increases slowly and ultimately becomes const. $Na_4P_2O_7$ and HF yield H_2PO_3F, but it remains undecided whether reaction is due to the P_2O_7 ion or whether hydrolysis precedes the change. KF and KH_2PO_4 do not react in dil. or conc. solution or in alkaline solution. The bimol. nature of the change $H_3PO_4+HF \rightleftharpoons H_2PO_3F+H_2O$ is established, but the equation is regarded as purely schematic, since in solutions of conc. H_3PO_4 and HF very different types of mols. and ions are present which exert mutual influence.
H. Wren.

Theory of the sulphuric acid chamber reaction. W. J. Müller.—See B., 1932, 20.

Dehydration of selenious acid. N. Rae (J.C.S., 1931, 3342—3343).—H_2SeO_3 when kept over P_2O_5 at room temp. is converted (completely in 50 days) into SeO_2.
C. W. Davies.

Chromium halides. II. System chromium–iodine. Preparation and behaviour towards hydrogen of chromous iodide. F. Hein and I. Wintner-Hölder (Z. anorg. Chem., 1931, **202**, 81—98).—Pure CrI_2, m. p. 790—795°, has been prepared by heating electrolytic Cr with an excess of I in N_2 or vac. at 1150—1200°, and removing the excess of I from the product by heating at 200°. Two forms, viz., greyish-white and dark brown, exist. CrI_2 has an appreciable decomp. pressure at 400—700°, but in presence of a trace of I vapour this is strongly depressed, and rises only very slowly with rise of temp. I reacts with CrI_2, although not very readily, at 300°, but a product containing more than 91% of CrI_3 could not be obtained. I reacts vigorously with pyrophoric Cr at 300°, with partial formation (67%) of CrI_3. Attempts to obtain decomp. pressure–temp. curves for the two iodides are described.
H. F. Gillbe.

Action of hydrogen sulphide on chromates. II. Hydrogen chromate. H. B. Dunnicliff and G. S. Kotwani (J. Physical Chem., 1931, **35**, 3214—3236; cf. A., 1929, 282).—When H_2S is passed into aq. CrO_3 the solution becomes dull purple, then dark brown, when it contains colloidal S and $Cr(OH)_3$, $Cr^{\cdots}$, sulphate, and CrO_3. The sulphate is initially ionic, but after a time half of it has become co-ordinated, and after further action of H_2S a brown solid containing a co-ordinated sulphatochromium sulphate together with S and $Cr(OH)_3$ separates, the $Cr(OH)_3$ reacting with CrO_3 to form an oxide Cr_5O_9 or CrO_2. The liquid phase then contains SO_4'', $Cr(OH)_3$, CrO_3, and colloidal S. After prolonged passage of H_2S the solid phase becomes pale green, containing one or more co-ordinated Cr sulphates, $Cr_2(S_2O_3)_3$ (probably co-ordinated), S, and $Cr(OH)_3$, whilst the only ion in the liquid is HS′ or S″.
L. Kelley (*c*).

Synthesis of chromic thiocyanate complexes of heavy metals. D. M. Tsamados and A. C. Bouzuazou (Praktika, 1929, **4**, 113—117; Chem. Zentr., 1931, ii, 208).—The *compounds* $Bi[Cr(CNS)_6]$ and $Sb[Cr(CNS)_6],H_2O$ are described.
A. A. Eldridge.

Bromine pentafluoride. O. Ruff and W. Menzel (Z. anorg. Chem., 1931, **202**, 49—61).—*BrF_5*, m. p. −61·3°, b. p. 40·5°, has been prepared by heating BrF_3 with F_2 at 200°; the reaction is complete and the yield is about 87·5%. At room temp. BrF_5 is a colourless fuming liquid having d 3·496—0·00346T; the v. p. is given by $\log_{10} p=8{\cdot}0716-1677{\cdot}7/T$. It reacts explosively with H_2O, but the controlled reaction results in the production of, probably, $BrOF_3$; with NaOH solution, NaF, $NaBrO_3$, NaBr, and O_2 are formed. The behaviour of a mixture of BrF_5 and Br on distillation suggests that a fluoride lower than BrF_3 exists. The action of BrF_5 on many elements and some compounds is described.
H. F. Gillbe.

Manganic dithiocarbamates. L. Cambi and A. Cagnasso (Atti R. Accad. Lincei, 1931, [vi], **14**, 71—74).—The prep. and properties of the following *manganic dithiocarbamates* are described: $(C_5H_{10}NCS_2)_3Mn$; $[(C_4H_9)_2NCS_2]_3Mn$; $[(C_7H_7)_2NCS_2]_3Mn$. They are very analogous to those of the corresponding Fe^{III} compounds.
O. J. Walker.

Potassium rheni-iodide. H. V. A. Briscoe, P. L. Robinson, and A. J. Rudge (J.C.S., 1931, 3218—3220).—Potassium per-rhenate with excess of KI and boiling aq. HI gives on cooling the *compound* K_2ReI_6. This is hydrolysed by H_2O, but can be recryst. in solvated form from $COMe_2$. It is quite stable up to 200°, but above 300° in dry N_2 the quant. reaction $K_2ReI_6 \longrightarrow 2KI+Re+4I$ occurs.
C. W. Davies.

Tervalent rhenium and its behaviour on oxidation. W. Manchot, H. Schmid, and J. Düsing (Ber., 1931, **64**, [*B*], 2905—2908; cf. A., 1931, 810).—Reduction of K_2ReCl_6 by Zn and acid or in H_2SO_4 at a Hg cathode affords evidence of the existence of Re^{III}. With air or O_2 the solution thus obtained gives dark, wine-red liquids in which Re^{V} appears present. In acid solution K_2ReCl_6 does not bleach indigotinsulphonic acid or reduce $KMnO_4$, whereas in alkaline solution it is readily autoxidised. The crude brown product obtained by Enke (*loc. cit.*) behaves towards oxidation and reduction like K_2ReCl_6.
H. Wren.

Ferromagnetic ferric oxide. A. Girard and G. Chaudron (Compt. rend., 1931, **193**, 1418—1421). —Magnetisation–temp. curves are given for lepidocrocite (*a*) natural, or prepared (*b*) by slow oxidation of $Fe(OH)_2$, (*c*) by hydrolysis of $NaFeO_2$, (*d*) by rusting Fe in a saline solution, in air, and in vac. In air (*b*) is dehydrated at about 250°, and transformed from ferromagnetic into stable Fe_2O_3 at 525°. (*c*) is dehydrated at about 140° with formation of a more stable ferromagnetic Fe_2O_3 unchanged at 600°. In vac. (*a*), (*b*), and (*d*) are dehydrated at about 250°; the Fe_2O_3 then begins to dissociate with formation of Fe_3O_4 (cf. A., 1930, 1100; 1931, 324).

C. A. Silberrad.

Differentiation of the various forms of ferric oxide and hydrated oxide. III. Hydrated ferric oxide from iron pentacarbonyl. W. H. Albrecht and E. Wedekind (Z. anorg. Chem., 1931, **202**, 205—208).—$Fe(OH)_3$ may be prepared by treating a solution of $Fe(CO)_5$ in Et_2O with aq. H_2O_2 and extracting the mixture with H_2O; traces of $Fe(CO)_5$ may be removed with Et_2O. The yellow product obtained on ultra-filtration is the α-hydrate; on ageing by heating at 100° with H_2O it becomes red, the lattice begins to break down, and the magnetic susceptibility increases considerably. The prep. was free from Fe^{II}, and the aged product presumably contained other hydrates of unknown structure.

H. F. Gillbe.

Metal carbonyls. X. Iron carbonyl halides. W. Hieber. **1. Substitutions in iron tetracarbonyl halides** [with G. Bader and K. Ries]. **2. Trimeric iron carbonyl bromide** [with E. Becker] (Z. anorg. Chem., 1931, **201**, 329—336; cf. A., 1931, 1255).—1. $Fe(CO)_4I_2$ reacts at 30° with $EtS{\cdot}[CH_2]_2{\cdot}SEt$ to give the *compound* $(EtS{\cdot}[CH_2]_2{\cdot}SEt)Fe(CO)_2I_2$. Both this and the corresponding *bromide* form red crystals. The *chloride* is decomposed at −10° with total loss of CO. With *o*-phenanthrolin cryst. *dicarbonyl*-o-*phenanthrolin ferrous bromide* has been prepared, the *chloride* being formed only below −10°.

2. $[Fe(CO)_4]_3$ reacts with excess of Br at 0° to give a mixture of 3 mols. of $Fe(CO)_4Br_2$ with 1 mol. of the *compound* $[Fe(CO)_3Br_2]_3$. The analogy of the carbonyl ferrous halides with the corresponding Pt^{II} compounds is discussed.

F. L. Usher.

Metal carbonyls. XI. Iron carbonyls substituted by ethylenediamine and a new mode of formation of iron carbonyl hydride. W. Hieber and F. Leutert (Ber., 1931, **64**, [*B*], 2832—2839; cf. A., 1931, 1255).—Ethylenediamine monohydrate and $Fe(CO)_5$ react readily according to the scheme: $Fe(CO)_5+C_2H_4(NH_2)_2,H_2O=Fe(CO)_4H_2+NH_2{\cdot}C_2H_4{\cdot}NH{\cdot}CO_2H$, reaction ceasing at room temp. after separation of the carbamic acid. $Fe(CO)_4$ and $C_2H_4(NH_2)_2$ immediately evolve gas and yield a dark red solution. Reaction depends on the disproportionations $2Fe(CO)_4=Fe(CO)_5+Fe(CO)_3$ and $3Fe(CO)_4=Fe(CO)_5+2Fe(CO)_3+CO$, these changes being facilitated since $Fe(CO)_5$ reacts with the diamine (see above) and $Fe(CO)_3$ is stabilised by it. In a similar manner compounds containing $Fe(CO)_2$ can arise from $Fe(CO)_4$ and $Fe(CO)_3$, thus $2Fe(CO)_4=Fe(CO)_5+Fe(CO)_2+CO$ and $3Fe(CO)_3=Fe(CO)_5+2Fe(CO)_2$. Addition of H_2O to the red solution at 40° causes pptn. of the *compound* $Fe_4(CO)_{12}\,en_3$, immediately decomposed by air to $Fe(CO)_4$, FeO, and $C_2H_4(NH_2)_2$. In absence of O_2 decomp. occurs with pptn. of the stable $Fe_2(CO)_5\,en_2$. If a mixture of $Fe(CO)_4$ and $C_2H_4(NH_2)_2$ is heated at 60—80°, the compound $Fe_2(CO)_5\,en_2$ separates, whilst $Fe(CO)_5$, simultaneously produced, undergoes the "base reaction." Up to this stage, only CO is evolved, whereas at higher temp. the gas is accompanied by H_2 in consequence of the auto-decomp. of the hydride, $2Fe(CO)_4H_2=Fe(CO)_5+Fe(CO)_3+2H_2$. The final result of the reactions is that only $Fe(CO)_2$ compounds remain in solution at 145° which cannot be further degraded without complete decomp. and separation of Fe. The isolation of the *compounds* $Fe_4(CO)_{12}\,en_3$ and $Fe_2(CO)_4\,en_3$ is described. Treatment of the last-named substance with dil. acids proceeds according to the equation $Fe_2(CO)_4\,en_3+8H^{+}+Fe(CO)_4H_2+Fe^{++}+3(en\,.\,2H^{++})$. The volatile *hydride* is condensed at −180°. At room temp. or when passed through EtOH or glycerol it is decomposed: $2Fe(CO)_4H_2=Fe(CO)_5+Fe(CO)_3+2H_2$.

H. Wren.

Phosphides of heavy metals. II. Action of hypophosphite on nickel and cobalt salts. R. Scholder and H. L. Haken (Ber., 1931, **64**, [*B*], 2870—2877).—Reaction between Ni salts and hypophosphite occurs only in neutral or alkaline solution, leading to mixtures of Ni and Ni phosphides, the composition of which varies greatly with experimental conditions. The P content of the product is at a max. when the final solution is acid. Contrary to Paal (A., 1931, 1374), the products are ultimately sol. in boiling HCl or AcOH. Cautious treatment with HCl leaves Ni_2P as a definite compound, whereas treatment with AcOH leaves Ni_5P_2, transformed by HCl into Ni_2P. Dissolution of Ni_2P in HCl occurs according to the equation $Ni_2P+4HCl+3H_2O=2NiCl_2+H_3PO_3+7H$. The Ni–P compounds cannot be regarded as true phosphides, but are intermetallic substances. Reaction between Co salts and hypophosphite almost invariably occurs in initially neutral or alkaline solution, provided the concn. of the hypophosphite is sufficiently great, although the yields from neutral solutions are very small in consequence of the solvent action of the liberated acid. Hence $Co(OAc)_2$ is more suitable than the Co salts of strong acids. In alkaline solution in presence of KCN neither Co nor Ni is pptd. The best yields of a mixture of Co and Co phosphide is obtained by the action of KH_2PO_2 on a solution of KOH, K tartrate, and $Co(OAc)_2$ in H_2O. The mixtures are magnetic, more or less readily autoxidised, and retain H_2O tenaciously. Reaction with HCl gives $CoCl_2$, H_3PO_3, and H_2; PH_3 is produced at most in traces. Restricted action of acids causes very marked enrichment of the residues in P. The existence of intermetallic compounds CoP, Co_3P, and Co_4P or Co_5P is probable.

H. Wren.

Indirect analysis. E. Rinck (Bull. Soc. chim., 1931, [iv], **49**, 1465—1467).—The indirect analysis of a mixture of constituents which cannot be quantitatively separated (*e.g.*, K, Rb, Cs) is impossible when their number exceeds two, since the system of equations obtained is indeterminate.

C. W. Davies.

Condensation gas analysis and its extension to adsorption in silica gel at low temperature. G. KUHN.—See B., 1932, 7.

Testing the reaction of distilled water. E. TRUOG (Science, 1931, 74, 633—634).—Pure H_2O in equilibrium with the atm. has p_H 5·6—5·8. The amount of acid, and especially NH_3, in laboratory air may be high enough profoundly to modify the p_H of distilled H_2O. Neutral bromocresol-purple is an excellent indicator for testing the p_H of distilled H_2O by the method described. In the absence of CO_2 and NH_3 the p_H of pure H_2O rises to 7.
L. S. THEOBALD.

Conductometric studies. II. Influence of alcohol in conductometric titrations and on indicators. W. POETHKE (Z. anal. Chem., 1931, 86, 399—422; cf. A., 1931, 1256).—Corrections to be applied in the titration of a weak acid with NaOH in the presence of different proportions of neutral EtOH have been determined for naphthol-, phenol-, and thymol-phthalein as indicators. The first-named is the most suitable. The effect of neutral salts has also been studied. In conductometric titrations EtOH does not affect the "neutrality" point, but the latter is sensitive to neutral salts, especially when the concn. of EtOH is high. F. L. USHER.

Simple method of conductometric titration. N. RAE (J.C.S., 1931, 3143—3147).—The "Dionic" Water Tester replaces the usual electrical equipment.
C. W. DAVIES.

Measurement of p_H of liquids by means of a rotating electrode. P. L. DU NOÜY (Compt. rend., 1931, 193, 1417—1418).—Hasselbach's (cf. A., 1911, ii, 182; 1913, ii, 379) and Clark's (cf. A., 1916, ii, 75) methods are modified by giving the electrode the form of a rotating disc (300—400 r.p.m.) half in the liquid and half in H_2. C. A. SILBERRAD.

Solutions for colorimetric standards. V. Systems proposed for use in the determination of p_H values. J. P. MEHLIG and M. G. MELLON (J. Physical Chem., 1931, 35, 3397—3414; cf. A., 1931, 699).—The light transmitted by solutions of various org. indicators and mixed solutions of coloured inorg. salts recommended as colorimetric standards in p_H determinations has been analysed spectrographically. The results show that solutions containing Co, Fe, and Cu salts are not satisfactory as standards for comparison with solutions of two-colour indicators, for an exact match cannot be obtained, and different observers may therefore arrive at different results. Mixtures of K_2CrO_4 and $K_2Cr_2O_7$ may, however, be used in conjunction with one-colour indicators, such as the nitrophenols, if proper precautions are taken.
W. T. HALL (c).

Salicylic acid as an alkalimetric standard. J. ROSICKÝ and J. TAMCHYNA (Chem. Listy, 1931, 25, 468—470).—Salicylic acid is preferred to $H_2C_2O_4$ or BzOH for the standardisation of alkali solutions.
R. TRUSZKOWSKI.

Determination of fluorine in phosphate rock and phosphatic slags. D. S. REYNOLDS and K. D. JACOB.—See B., 1932, 62.

Portable motor-driven impinger unit for determination of sulphur dioxide. R. B. SMITH and B. S. T. FRIIS (J. Ind. Hygiene, 1931, 13, 338—342).—Apparatus for scrubbing a known vol. of air through NaOH solution for subsequent iodometric determination of SO_2 is described. F. L. USHER.

Exact determination of very small quantities of gases containing sulphur (H_2S, SO_2, and CS_2) in the atmosphere when present together. J. BÖESEKEN and H. D. MULLER (Rec. trav. chim., 1931, 50, 1117—1124).—The air is passed through three 1-dm. tubes containing respectively: finely-divided AgCl deposited on asbestos, to retain H_2S; porous stone impregnated with MnO_2, to retain SO_2, and porous stone impregnated with NaOEt, to retain CS_2. The tubes are then heated separately in a stream of H_2 containing a little HCl, the S is converted into H_2S by ter Meulen's method and is determined with I. An accuracy of 0·01 mg. S per cu. m. is claimed, and is independent of the degree of dilution. For determining total S only, the third tube alone suffices. C. W. DAVIES.

Determination of sulphate ions in water analysis. E. ROTHENBACH and H. ANTELMANN.—See B., 1932, 50.

Volumetric determination of sulphuric acid in water. B. PASCHKE.—See B., 1932, 50.

Oxidation of hydrothiocyanic acid by permanganate. W. ILLARIONOV (Z. anal. Chem., 1931, 87, 26—32).—The chief source of error in the titration of HCNS with aq. $KMnO_4$ in presence of H_2SO_4 is the loss of HCNS by the formation of a volatile complex with the HCN produced by the reaction. In calculating the result an experimentally determined decomp. coeff. should be employed. In presence of CN′ nearly all the $KMnO_4$ should be added at once and the titration completed by the addition of a further 3 or 4 drops. The same decomp. coeff. as before is then required. M. S. BURR.

Determination of ammonium salts by the formaldehyde method. E. SORRENTINO (Atti III. Cong. Naz. Chim. pura Appl., 1929, 552—556; Chem. Zentr., 1931, ii, 279).—To 20—25 c.c. of solution (1 g. of salt) are added 5 c.c. of neutralised 40% CH_2O solution; titration is carried out with $0{\cdot}2N$-$Ba(OH)_2$ in presence of phenolphthalein. The free acid is titrated in a control using Me-red.
A. A. ELDRIDGE.

Determination of phosphorous and of hypophosphorous acid. L. WOLF and W. JUNG (Z. anorg. Chem., 1931, 201, 337—346).—Both H_3PO_3 and H_3PO_2 are oxidised by I in acid solution, whereas in $NaHCO_3$ solution only H_3PO_3 is oxidised. On this basis an iodometric method, which permits the two acids to be determined separately or when mixed, has been devised. $H_4P_2O_6$ exercises no disturbing effect. F. L. USHER.

Argentometric method for determining hypophosphoric acid in presence of phosphates or phosphites. L. WOLF and W. JUNG (Z. anorg. Chem., 1931, 201, 347—352; cf. preceding abstract).—At p_H 1—2 Ag_3PO_4 is sol. and reduction of Ag salts by H_3PO_3 inappreciable, whereas $H_4P_2O_6$ is quantitatively pptd. by excess of Ag˙. A method for determining $H_4P_2O_6$, which is pptd. by excess of

$AgNO_3$ from a solution acidified with H_3PO_4 or HCO_2H, is described. F. L. Usher.

Determination of phosphorous, hypophosphorous, hypophosphoric, and phosphoric acids. L. Wolf and W. Jung (Z. anorg. Chem., 1931, **201**, 353—360; cf. preceding abstracts).—All four acids when present together can be determined only by separating H_3PO_2 from the mixture before determining $H_4P_2O_6$. This is done by adding excess of $Ba(NO_3)_2$ to the neutral solution and separating the sol. $Ba(H_2PO_2)_2$. The methods already described may then be applied. F. L. Usher.

Elimination of the phosphate ion as $Pb_3(PO_4)_2$. J. Bougault and E. Cattelain (Compt. rend., 1931, **193**, 1093—1095).—The method, which enables phosphates to be removed from a solution containing Mn, Mg, Ca, Sr, and Ba, consists in adding aq. $Pb(OAc)_2$ to the solution under investigation acidified with AcOH, the Pb remaining in solution being then removed. C. A. Silberrad.

Modified Gutzeit apparatus. G. H. Davis (Food Tech., 1931, **1**, 145).—A H_2O jacket allows only dry AsH_3 to pass to the $HgCl_2$ paper. E. B. Hughes.

Arsenic testing by Gutzeit method. L. Pointing (Food Tech., 1931, **1**, 146).—A scrubbing device removes H_2S from the AsH_3 and a brass union grips the $HgCl_2$ paper to localise the stain. E. B. Hughes.

Determination of carbon dioxide. C. J. Schollenberger (Chemist Analyst, 1931, **20**, No. 5, 10—14).—The carbonate is decomposed with dil. acids in an evacuated apparatus, the CO_2 being passed into standard $Ba(OH)_2$, the excess of which is determined titrimetrically (thymolphthalein). Chemical Abstracts.

Oxidimetric determination of sodium. H. Gall and K. H. Heinig (Z. anorg. Chem., 1931, **202**, 154—160).—The Na is separated as Na U Zn acetate, which is dissolved in dil. H_2SO_4 and filtered through a 6-cm. layer of electrolytic Cd to reduce the U^{VI}. Since up to 3% of the U may thus be reduced to U^{III}, the solution is then filtered, with free exposure to the air, to convert the U^{III} into U^{IV}. The solution is finally titrated with $0{\cdot}1N$-$KMnO_4$. The error, with about 5 mg. NaCl, is about $\pm 0{\cdot}5\%$. The method has the advantage that in the ppt. the U : Na ratio is always 3 : 1 and is not influenced by variations of the H_2O content. H. F. Gillbe.

Determination of potassium. R. K. Kuznetzova and M. F. Zagorski (Udobr. Urozhai, 1931, **3**, 364—370).—The K_2PtCl_6 is reduced with Mg in boiling aq. solution. Chemical Abstracts.

Determination of small quantities of potassium. C. F. Miller (Chemist-Analyst, 1931, **20**, No. 5, 8—10).—K_2PtI_6 is formed from K_2PtCl_6 and KI and is determined colorimetrically in presence or absence of EtOH. For 50 in 10^6 the error is $\pm 5\%$. NH_4 salts, org. matter, and a large excess of acid must be absent. Chemical Abstracts.

Volumetric method of determining potassium. Austerweil and Lemay (Bull. Soc. chim., 1931, [iv], **49**, 1541—1542).—The ppt. with Na cobaltinitrite is dissolved in dil. HCl and the solution exactly neutralised; the Co is then pptd. with standard Na_2CO_3 and determined by a back-titration, after filtering, with HCl. C. W. Davies.

Determination of magnesia and alkalis after decomposition by hydrofluoric acid. F. Bann (Glashütte, 1931, **61**, 170—171; Chem. Zentr., 1931, i, 2523).—The substance decomposed by HF is evaporated, taken up with HCl, and the heavy metals and CaO are determined as usual. Mg is pptd. with alkali-free, yellow HgO, the alkalis are weighed as sulphate and then separated by the perchlorate method. L. S. Theobald.

Volumetric determination of copper. A. Malkov (J. Chem. Ind. Russ., 1931, **8**, No. 13, 44—46).—1—2 c.c. of solution are kept for 20—25 min. at room temp. with $0{\cdot}5$—$1{\cdot}0$ c.c. of a solution containing 20 g. of K Na tartrate and 15 g. of KOH per 100 c.c., and with 1—3 c.c. of 1% fructose or invert-sugar, the washed ppt. of Cu_2O is dissolved in 20—30 c.c. of a solution containing 5 g. of $Fe_2(SO_4)_3$ and 20 g. of H_2SO_4 per 100 c.c., and Cu is determined by titration with $KMnO_4$. This method can be applied in the presence of Pb, Sn, Fe, and Zn, when $\not< 5$ mg. of Cu are present. R. Truszkowski.

Gravimetric determination of aluminium by the cyanate method. Separation from manganese and zinc. A. Okáč (Publ. Fac. Sci. Univ. Masaryk, 1931, No. 135, 1—5).—The results given by Ripan's method (A., 1928, 499) are about 2% higher than the actual vals. The method can be applied in the presence of Mn and Zn provided that a considerable excess of NH_4Cl be present. R. Truszkowski.

Precipitation of manganese as dioxide and its use in quantitative separations. K. A. Jensen (Z. anal. Chem., 1931, **86**, 422—438).—An exhaustive study of the sorption of foreign metals by MnO_2 pptd. from acid solution by persulphates under various conditions shows that the method cannot be used for quant. separation of Mn from other metals, with the exception of Cr, Mg, Be, Al, and the alkali metals. F. L. Usher.

Determination of manganese with potassium periodate. C. F. Miller (Chemist-Analyst, 1931, **20**, No. 5, 8).—The sample is dissolved in a mixture of conc. H_2SO_4 (15 c.c.), HNO_3 (20 c.c.), H_3PO_4 (10 c.c.), and H_2O (to 100 c.c.); $0{\cdot}2$—$0{\cdot}4$ g. KIO_4 is added, the solution is boiled for 1 min., heated for 5—10 min. at 100°, and cooled, the MnO_4' being determined colorimetrically. Chemical Abstracts.

Determination of manganese. R. G. Harry (J.S.C.I., 1931, **50**, 434—436T).—A review of the following methods is given: gravimetric (oxide, sulphide, sulphate, and pyrophosphate); volumetric (chlorate, Pattinson, persulphate, Volhard, bismuthate, and red lead); and colorimetric [$(NH_4)_2S_2O_8$, tetramethyldiaminodiphenylmethane, and KIO_4].

Determination of manganese by Knorre's method. R. G. Harry (J.S.C.I., 1932, **51**, 24T).—Knorre's method (A., 1902, ii, 108) in which the Mn is oxidised by means of $(NH_4)_2S_2O_8$ and pptd.

as hydrated MnO_2 was investigated in the presence of other metals equiv. in amount to 4% of each. In the presence of Cu, Pb, Zn, and Ca the method was entirely suitable. Ti, Sn, and Co seriously interfere; Bi, Sb, As, V, Cr, and Ni interfere to a small extent.

Use of zinc oxide in determination of cobalt and manganese. J. I. Hoffman (Bur. Stand. J. Res., 1931, **7**, 883—892).—The addition of ZnO to a solution obtained by dissolving steel in $HCl–HNO_3$ or $H_2SO_4–HNO_3$ will ppt. all the $Fe^{\cdots}$, W, V, Cr, U, Zr, Ti, Al, P, As, Sn, and nearly all the Cu, Mo, and Si. $Fe^{\cdot\cdot}$, W (if not previously oxidised), Cu, Mo, Sb, and Pb may be expected in the filtrate. Separation of Fe and certain other constituents of steel from Co and Mn by means of ZnO is satisfactory if double pptns. are made, but is not satisfactory for Ni. Small amounts of Na_2CO_3 in the ZnO are not objectionable and the temp. of pptn. has little influence. E. S. Hedges.

Colorimetric determination of iron in drinking and effluent waters by means of sulphosalicylic acid. L. N. Lapin and W. E. Kill.—See B., 1932, 50.

Use of bromate in volumetric analysis. VI. Determination of iron, using basic mercuric bromate. C. F. Smith and H. H. Bliss (J. Amer. Chem. Soc., 1931, **53**, 4291—4297; cf. A., 1931, 925).—The Fe^{III} solution is reduced at the b. p. with $SnCl_2$ in presence of HCl, avoiding excess of $SnCl_2$. There are added at room temp. $HgCl_2$, a mixed solution of $CuSO_4$, $(NH_4)_3AsO_4$, and H_3PO_4, and a solution of fuchsin, chrysoidine-R, Bordeaux, or naphthol-blue-black as indicator, and then $0{\cdot}1N$-$Hg(OH)BrO_3$ is run in until the colour of the indicator is discharged. MeOH, EtOH, $H_2C_2O_4$ and succinic, citric, and tartaric acids do not interfere. W. T. Hall (*c*).

Detection of traces of vanadium. F. Ephraim (Helv. Chim. Acta, 1931, **14**, 1266—1269).—In alkaline solution the reaction $V^{IV}+Fe^{\cdots} \rightleftharpoons V^{V}+Fe^{\cdot\cdot}$ proceeds from left to right. The solution in which V is sought is partly evaporated with HCl and to the cooled solution $FeCl_3$ and dimethylglyoxime solutions are added. On adding aq. NH_3 the depth of the red coloration produced is approx. proportional to the V content of the solution. The colour is transient, but may be preserved by covering the solution with, *e.g.*, ligroin. Extreme care must be taken to exclude oxidising agents. Few metals interfere, but Co, Ni, Fe, Mn, or Cu, if present in quantity, should be removed with NaOH; CrO_4'' interferes. The limiting concn. is 1 in 4×10^5. The oxidation of benzidine by NH_4 vanadate in AcOH solution provides a drop reaction for V, but the limiting concn. is only 1 in 2×10^4. V yields with cacotheline a bluish-violet colour; by the drop method the limiting concn. is 1 in $2{\cdot}5\times10^4$. H. F. Gillbe.

Determination of bismuth as metal. E. Rupp and G. Hamann (Z. anal. Chem., 1931, **87**, 32—35).—In the gravimetric determination of Bi the metal pptd. by alkaline aq. CH_2O may be obtained free from oxide if glycerol or Na K tartrate, preferably the former, is present. A short subsequent treatment with H_2 ensures accurate results. If Mg is used for pptn., Na K tartrate should be present to neutralise the HCl and prevent the formation of BiOCl. The latter method is much more tedious than the former. M. S. Burr.

High-temperature laboratory electric furnace. W. Weyl and M. Bichowsky (Chem. Fabr., 1931, 469).—The Pt or Pt–Rh heating element is wound on the inner surface of a tube of suitable refractory material; practically the whole of the heat radiated by the wire is thus utilised, and temp. of 1550—1600° may be attained and maintained const. for long periods. The apparatus is especially suitable for the study of, *e.g.*, silicates in an oxidising atm. H. F. Gillbe.

Measurement of very small thermal effects. W. Świentosławski (Ann. Chim., 1931, [x], **16**, 251—275).—Details are given of the adiabatic micro-calorimeters previously described (A., 1931, 593). Spurious thermal effects due, *e.g.*, to traces of adsorbed H_2O may be a source of serious error. Heats of adsorption of C_6H_6, EtOH, and CCl_4 by activated charcoal are given. Heats of vaporisation at 20° are: H_2O 581·1, C_6H_6 98·2, $CHCl_3$ 66·8±0·3% g.-cal. per g. (cf. *ibid.*, 553). Sp. heats of radioactive minerals are recorded. J. G. A. Griffiths.

Improved quartz mercury-vapour lamp. G. S. Forbes and L. J. Heidt (J. Amer. Chem. Soc., 1931, **53**, 4349—4350).—The lamp retains such advantages as operation under const. pressure, a highly conc. discharge, and ease of renewal without special vac. technique and eliminates cemented joints and objectionable capillaries used to check Hg oscillations. H. F. Johnstone (*c*).

Lustre-meter and spectrophotometer. H. Boffey and D. A. Derrett-Smith (J. Sci. Instr., 1931, **8**, 356—360).—With this instrument angles of reflexion and incidence can be varied over a wide range, and the sample tested need not be cut. C. W. Gibby.

Method of grazing incidence for the determination of indices of refraction. A. Biot (Ann. Soc. Sci. Bruxelles, 1931, **51**, 185—191).—To obtain max. accuracy, the line of sight must be within 5° of perpendicularity to the face of the prism. The method cannot give an accuracy of more than 0·00002 in *n*. C. W. Gibby.

Automatically constant monochromatic illumination from a spark source. G. S. Forbes and F. P. Brackett (J. Amer. Chem. Soc., 1931, **53**, 3973—3976).—The spark is formed between adjacent edges of two square bars supported at right angles to each other and moving in horizontal planes. Conduction and radiation of heat are so rapid that erosion is minimised, and the illuminating power is const. over long periods. H. F. Johnstone (*c*).

Automatic colorimetry. W. Kordatzki (Chem. Fabr., 1931, 485—486).—The apparatus automatically withdraws at regular intervals samples of solution for colorimetric control of p_H or for colorimetric testing for the presence of certain ions. The sample mixes with the indicator or testing solution and is then discharged automatically through a siphon. E. S. Hedges.

Double potentiometer for measurement of temperatures. C. Sălceanu (Bull. Acad. Sci.

Roumaine, 1931, **14**, 87—88).—A variable voltage, tapped off from a potentiometer, is applied to a second potentiometer, on which the e.m.f. of a thermocouple is balanced. Temp. between 0° and 300° can be measured to 0·2°. C. W. GIBBY.

Automatic p_H recorder. C. MORTON (J.S.C.I., 1931, **50**, 436—438T).—The solution under examination flows through a three-compartment cell, the e.m.f. of which fluctuates in unison with the changes in $[H^{\cdot}]$ and the voltage variations are continuously recorded in p_H units. The two end chambers, into which the electrodes are inserted, contain the solution under test and a reference buffer solution, respectively, and the central chamber contains saturated KCl solution. A concn. cell is thus formed. By means of siphoning devices the intermittent flushing of the three chambers is rendered automatic.

Apparatus for determination of electrical conductivity. W. MUCHLINSKY (Chem. Fabr., 1931, 462—464, 469—472).—The volume of sound at the balance point may be reduced by using a.c. mains, instead of a buzzer, as the source of e.m.f. Suitable circuits are described, including one in which thermionic valves are used to obtain a const. note of adjustable frequency, and one in which a valve is used as the generator. A circular bridge wire and scale is described. For determination of the balance point the telephone is too insensitive, and suitable a.c. instruments are expensive; the current should therefore be rectified. The method of using thermionic valves and " dry " rectifiers is described. If a valve amplifier also is used, a cheaper and more stable galvanometer may be employed. Methods of preparing and mounting Pt electrodes are noted. H. F. GILLBE.

Extraction apparatus for large quantities of solid material. F. FRIEDRICHS (Chem.-Ztg., 1931, **55**, 963).—The apparatus is made in sections with standard ground-glass joints, a jointed glass " chain " being included in the vapour tube for rigidity. Extraction vessels ranging in size from 30 c.c. to 20 litres are available. These are in two parts, for filling purposes, with a " stopper " or " plate " type ground-glass joint according to size. A simpler type of apparatus serves for cases where extraction may be performed in the hot and need not be exhaustive. S. S. WOOLF.

Laboratory rectifying stills of glass. J. H. BRUUN and S. T. SCHICKTANZ (Bur. Stand. J. Res., 1931, **7**, 851—882).—A set of all-glass rectifying stills, suitable for pressures between 1 atm. and about 50 mm., is described. The stills are provided with bubbling-cap columns containing 30—60 plates, and surrounded by a jacket provided with a series of independent electrical heating units in order to maintain adiabatic conditions. The reflux ratio may be adjusted and maintained const. A continuous b. p.-apparatus is incorporated in the receiving system for the purpose of obtaining the true b. p. of the distillates. A still of the packed-column type for distillations at pressures less than 50 mm. is also described. Efficiency tests are given. E. S. HEDGES.

Soda-lime tube substitute for standard solution bottles. A. B. KNOEBEL (Chemist Analyst, 1931, **20**, No. 5, 20—21).—Moist air is introduced through NaOH solution in the first of two U-tubes. CHEMICAL ABSTRACTS.

Drop recorder. O. S. GIBBS (Science, 1931, **74**, 549; cf. A., 1929, 1415; 1931, 1026). L. S. THEOBALD.

Device for holding ultra-filtration membranes. C. BREEDIS (Science, 1931, **74**, 635). L. S. THEOBALD.

Calculation of number and size distribution of spherical crystals in opaque materials by means of the circles obtained from a plane section. E. SCHEIL (Z. anorg. Chem., 1931, **201**, 259—264).—Mathematical. F. L. USHER.

Magnetic spectrograph for β-rays emitted by feebly radioactive substances. G. OCCHIALINI (Atti R. Accad. Lincei, 1931, [vi], **14**, 103—107).—The radioactive substance is placed on the inside wall of a flat cylindrical box at the centre of which a Geiger–Müller counter is placed coaxially. The pressure inside can be reduced to a suitable val., and the apparatus is placed in an electromagnetic field so that the lines of force are parallel to the axis of the cylinder. The velocity of the β-rays emitted by Rb is 0·62 *c*. O. J. WALKER.

Small slow-combustion pipette for gas analysis. H. L. HARDEN (J. Sci. Instr., 1931, **8**, 332).—Both leads to the Pt heating spiral enter in the same piece of glass tubing through a rubber bung at the bottom of the pipette. C. W. GIBBY.

Safety siphon. R. READMAN (J. Sci. Instr., 1931, **8**, 331).—The siphon is filled by squeezing a rubber bulb attached to a side tube at its highest point, the delivery end being closed by a tap. C. W. GIBBY.

Mercury pumps used in connexion with gas-analysis apparatus. K. MELLANBY (J. Sci. Instr., 1931, **8**, 330).—Hg is contained in a steel reservoir closed by a rubber diaphragm, and can be forced up by pressing on the latter with a plunger having coarse and fine screw movements. C. W. GIBBY.

Gas holder for delivering known volumes of a dry gas at atmospheric temperature and pressure. G. W. ELLIS (J. Sci. Instr., 1931, **8**, 316—319).—The construction of a calibrated glass gasometer is described. C. W. GIBBY.

Apparatus for comparing the rate of dissolution of solid substances. V. COFMAN (Chem. and Ind., 1931, 1057—1058).—The solid substance is placed in a perforated boat attached to a hydrometer and the rate of dissolution is measured by the rate of rise of the hydrometer in the liquid. The apparatus is useful for comparing the behaviour of different specimens of colloidal substances, *e.g.*, soap, and for measuring the rate of disintegration of compressed tablets. E. S. HEDGES.

Constant-pressure device for an autoclave. D. H. MATHESON (Chemist-Analyst, 1931, **20**, No. 5, 21—22).—An electrical device is described. CHEMICAL ABSTRACTS.

Determination of diffusion coefficients. H. Kroepelin (Sitzungsber. physikal.-med. Soz. Erlangen, 1930, **62**, 285—288; Chem. Zentr., 1931, ii, 141).—An apparatus is described. A. A. Eldridge.

Sedimentation method for determining particle sizes, using an automatic [photographic] recorder. C. G. Sumner (Trans. Faraday Soc., 1932, **28**, 20—27).—The technique of Lambert and Wightman (A., 1925, ii, 1194) is improved. C_6H_6 is used as index liquid, and the evaluation of results is simplified. J. G. A. Griffiths.

New high vacuum system. J. A. Becker and E. K. Jaycox (Rev. Sci. Instr., 1931, [ii], **2**, 773—784).—A vac. of 2×10^{-8} mm. Hg can be obtained by using an oil diffusion pump backed by a pressure of 10^{-1} mm. and a charcoal trap instead of liquid air. C. W. Gibby.

History of the discovery of the critical state. W. König (Ann. Physik, 1931, [v], **11**, 985—986).

Chinese alchemy. J. R. Partington (Nature, 1931, **128**, 1074—1075).—Historical. L. S. Theobald.

Geochemistry.

Composition of the escaping gases from the Baré Spring (Cameroons Protectorate). A. Lepape and M. Geslin (Bull. Soc. franç. Min., 1930, **53**, 274—278; Chem. Zentr., 1931, i, 2453).—The spring, temp. 27°, emits 2·7 cu. m. every 24 hr. The H_2O contains Fe and Ca H carbonates and gives a residue of 0·91 g. per litre. The gases consist of 99·50% CO_2, 0·05% O_2, 0% H_2, 0·00080% CH_4, 0·00013% of higher hydrocarbons, 0·438% N_2, 0·0091% A (+traces of Kr and Xe), and 0·00008% He+Ne. L. S. Theobald.

Gas-yielding wells in Hukagawa. N. Miyabe (Proc. Imp. Acad. Tokyo, 1931, **7**, 344—347).—The evolution of gas containing a high % of CH_4 by three wells in Tokyo is possibly connected with a depression in the tertiary stratum and a subsidence of the surface in the vicinity. N. H. Hartshorne.

Classification and chemical composition of mineral waters. W. Wernadski (Bull. Soc. franç. Min., 1930, **53**, 417—442; Chem. Zentr., 1931, i, 2453).—The geochemical rôle of H_2O is discussed. Three main groups, fresh, salt, and thermal water, are further subdivided according to their contained gases and other relationships. L. S. Theobald.

Radioactivity of waters from heights in the Vosges. R. Delaby, R. Charonnat, and M. Janot (Compt. rend., 1931, **193**, 1434—1436).—Measurements of the radioactivity of 8 springs at heights of 1008—1424 m. show amounts of radon varying from 0·83 to 63·51 mμc per litre, and 36·12 in the gases from one. Similar measurements for granites from the neighbourhood of some of the springs (1·5—17·5) show somewhat similar variations. Granite, quartz, felspar, mica, and amphibole from the Ballon d'Alsace gave 17·5, 12·5, 8, 23, and 15·5 mμc respectively, whilst the springs there gave 63·51 and 62·83. C. A. Silberrad.

Lead content of rocks. G. Hevesy and R. Hobbie (Nature, 1931, **128**, 1038—1039; cf. following abstract).—The recorded determinations of Pb in samples representing 220 rocks give an average val. of 16×10^{-6} g. Pb per g. of rock, a larger val. than the $7\cdot5\times10^{-6}$ g. previously accepted (J. Wash. Acad. Sci., 1914, **4**, 58). The greater part of rock-Pb is of non-radioactive origin; the higher Pb content of acid rocks, which compared with basic rocks also have a relatively high U and Th content, is due to the fact that Pb, like U and Th, has a marked affinity for siliceous magmas. A comparison of the Pb content of basic and ultrabasic rocks with that of meteorites shows that the silicate shell of the earth received only a moderate share of the total Pb available for partition, and that this uneven distribution has been compensated only slightly by the formation of Pb by radioactive disintegration. L. S. Theobald.

Lead content of rocks. A. Holmes (Nature, 1931, **128**, 1039—1040; cf. A., 1926, 449; 1929, 1263).—The significance of Hevesy and Hobbie's determinations (preceding abstract), which show that the previous val. of $7\cdot5\times10^{-6}$ g. per g. rock is no longer representative, is discussed. These results show that the total Pb in composite rocks is from 4 to 53 times that of the generated Pb. Considerations of at. wt. for Pb in granitic rocks show that there is no reason to doubt the conclusion that Pb ores have been derived from granitic and related magmas, provided that the age of the earth is not considerably greater than 16×10^8 years. L. S. Theobald.

Radium in rocks. IV. Location and association of radium in igneous rocks. C. S. Piggot and H. E. Merwin (Amer. J. Sci., 1932, [v], **23**, 49—56; cf. A., 1929, 1035; 1931, 332).—The fractionation of a granite from Stone Mountain, Georgia, and of another from North Jay, Maine, both of high Ra content, showed that the Ra is associated much more with the micas than with the other components of the rock. The reason for this is not clear. Hot H_2O removes some of the emanation, but apparently neither the Ra nor the U, from most powdered specimens. The radioactivity is completely restored after 30 days. N. H. Hartshorne.

Actinium problem. G. Elsen (Chem. Weekblad, 1931, **28**, 714; cf. A., 1931, 1145).—The U contents and activities of certain minerals are recorded and discussed. H. F. Gillbe.

Probertite from Ryan, Inyo Co., California. W. F. Foshag (Amer. Min., 1931, **16**, 338—341).—Probertite contains CaO 15·88, MgO 0·06, Fe_2O_3+Al_2O_3 0·38, Na_2O 9·00, B_2O_3 49·10, H_2O 25·64, insol. 0·20, total 100·26%; it has H about 3½, d 2·135, n_α 1·517, n_β 1·525, n_γ 1·544. Chemical Abstracts.

Krausite. W. F. Foshag (Amer. Min., 1931, **16**, 352—360).—The mineral, found with alunite, coquimbite, and in a transition zone between the latter and roemerite, voltaite, etc., contains insol. 0·92, CaO 0·12, FeO 0·24, Fe_2O_3 24·94, K_2O 14·71, Na_2O 0·64, SO_3 51·05, SiO_2 2·19, H_2O 5·59, total 100·40%, corresponding with $K_2SO_4,Fe_2(SO_4)_3,2H_2O$. It has *d* 2·849, *H* 2·5; n_α 1·588, n_β 1·650, n_γ 1·722.

Chemical Abstracts.

Castanite. A. F. Rogers (Amer. Min., 1931, **16**, 396—404).—Castanite, from Knoxville, California, triclinic, contains Fe_2O_3 34·74, SO_3 35·11, H_2O 30·31, insol. 0·22, total 100·21%; $Fe_2O_3,2SO_3,8H_2O$. It has n_α 1·553, n_β 1·643, n_γ 1·657.

Chemical Abstracts.

Peculiarities of primary platinum ores from the Ural. A. G. Betechtin (Gorni Zhur., 1930, **106**, No. 1, 152—161).—The composition range of 14 ores was Pt 55·75—77·87, Fe 10·86—14·97, Cu 0·50—11·43, Ir 1·08—7·20, Ni 0·27—3·70%, with a little Pd, Rh, Ru, and Au. An increase in Ir is followed by a decrease in Cu; the same holds for Ni and Fe, but the Pt content does not decrease as Ir accumulates. Pt containing Cu exists in at least two modifications: admixture, and a Cu–Pt alloy on the outside of the Pt. Chemical Abstracts.

Plateau basalt of west Greenland. H. Nieland (Chem. Erde, 1931, 6, 591—612).—Petrographical descriptions and chemical analyses are given of an anorthoclase-trachyte and a picritic olivine-basalt from Svartenhuk. The differentiation of basaltic magma into andesitic and trachytic series is discussed. L. J. Spencer.

Geochemical rôle of sorption. W. Noll (Chem. Erde, 1931, 6, 552—577).—The geochemical distribution of elements in the cycle of sedimentary rocks is governed more by the sorption properties of colloids than by the sizes of ions, as in cryst. rocks.

L. J. Spencer.

Green-earths of southern Tyrol and other halmyrolytic iron silicates. K. Hummel (Chem. Erde, 1931, 6, 468—551).—The occurrences of green-earth between augite-porphyrite and Triassic limestone at Schlern and of celadonite between basalt and Eocene limestone at Monte Baldo are described in detail, with chemical analyses and optical determinations. These are compared with glauconite, chamosite, and other green chlorite-like minerals, and it is concluded that they have been formed by the submarine alteration of igneous rocks—a process which the author in 1922 named halmyrolysis. Owing to metamorphism, the green-earths of different geological periods show different characters and different refractive indices. L. J. Spencer.

Metamorphism of the ancient crystalline rocks of the Eastern Alps. H. Wieseneder (Tsch. Min. Petr. Mitt., 1931, 42, 136—181).—The cryst. schists where intruded by the Aspang granite have undergone certain modifications. A so-called eclogite is an altered amphibolite, and the so-called diabase is a diorite-like differentiation product of the granite. Enstatite- and anthophyllite-olivine-rocks have been formed by the interaction of amphibolites and dolomite-marbles. L. J. Spencer.

Amphibolites of the southern Odenwald and their relation to diorites and granites. V. Leinz (Tsch. Min. Petr. Mitt., 1931, **42**, 81—135).—Detailed petrographical descriptions with chemical analyses of these rocks are given. The amphibolites have been derived from diabase-tuffs, and are modified where they have been intruded by diorite and granite.

L. J. Spencer.

Bixbyite from Chubut [Argentina]. H. Corti (Anal. Asoc. Quim. Argentina, 1931, **19**, 109—116).—Analyses of various specimens are given; the composition varied between $3FeO,2MnO_2$ and $4FeO,3MnO_2$, with 2—4% of TiO_2. Other properties resembled those of bixbyite. H. F. Gillbe.

Chemical and mineralogical composition of the rock of Pic de Teide. E. Jérémine (Bull. Soc. franç. Min., 1930, **53**, 210—215; Chem. Zentr., 1931, i, 2453).—The Alca Vista rock, described by Preiswerk as a soda-trachyte, is a phonolite; the other rocks of the Pic de Teide are phonolitic. L. S. Theobald.

Identity of plancheite and shattuckite. Bisbeeite and katangite. A. Schoep (Bull. Soc. franç. Min., 1930, **53**, 375—393; Chem. Zentr., 1931, i, 2452—2453).—Plancheite from Katanga occurs in 3 different types and a formula cannot be given. Type 1, bluish-black with blue lustre, has the composition 36·03—36·63% SiO_2, 57·44—57·81% CuO, and 5·42—6·74% H_2O; hardness 6—7, *d* 3·94, n_γ 1·811, and n_α 1·730. Shattuckite, 37·91% SiO_2, 55·31% CuO, and 5·83% H_2O, n_γ 1·815 and n_α 1·752, is identical with this type. Type 2, light blue, hardness 2—3, *d* 3·2—3·3, n_γ 1·700—1·725, n_α 1·640—1·665, contains more H_2O, less CuO, and some CaO. Type 3, n_γ 1·660—1·685, n_γ 1·525—1·665, contains no CaO, more CuO, and also Al_2O_3 and Fe_2O_3. Bisbeeite from Arizona is identical with this type. Katangite is a gel of hydrated Cu silicate which has the same composition and properties as chrysocolla, with which it is identical. L. S. Theobald.

Natural and artificial ultramarines. F. M. Jaeger (Bull. Soc. franç. Min., 1930, **53**, 183—209; Chem. Zentr., 1931, i, 2447—2448).—The ultramarines are stable towards alkalis but unstable towards acids. Na can be replaced by Li (bluish-violet), Rb, Cs, K, Tl (violet), Ag (light yellow), Mg (light blue), and other bivalent metals (colourless) by treatment in aq. solution at 100—120°. Replacement of S by Se or Te yields blood-red or yellow ultramarines, respectively. They possess hydraulic properties and resemble permutits in many respects. The substitution of Na by Ag leads to an equilibrium dependent on concn. and temp., and that of Ag by alkali goes more readily with iodides than with chlorides. Replaceability and reaction velocity increase with a decrease in at. wt. of the alkali metal. All these ultramarines yield spectrograms identical with those of nosean and hauynite. The centred cubic lattice has *a* 9·13 Å. The space groupings of the atoms certain of which appear to be " wanderers " are discussed.

L. S. Theobald.

Formulæ of hauynite and cancrinite. L. H. Borgström (Bull. Comm. géol. Finlande, 1931, No. 92, 51—57; Chem. Zentr., 1931, ii, 30).—If it is assumed that the Ca atom is replaced by Na instead of by Na_2, the formula and analysis are in accord. The nosean mol. then has the composition

$3Na_2Al_2Si_2O_8,Na_2SO_4$. Na cancrinite has the formula $3Na_2Al_2Si_2O_8,Na_2CO_3$, and Ca cancrinite the formula $3Na_2Al_2Si_2O_8,2CaCO_3$; the two mols. form mixed crystals in all ratios. A. A. ELDRIDGE.

Elements and minerals of pegmatitic rocks. V. M. GOLDSCHMIDT (Nachr. Ges. Wiss. Göttingen, 1930, 370—378; Chem. Zentr., 1931, ii, 213).—A discussion. Besides distribution in magma according to SiO_2 content, there is also distribution according to the ratio Na+K : Al. A. A. ELDRIDGE.

Asphalt ring from Ur of the Chaldees. J. F. HACKFORD, S. LAWSON, and P. E. SPIELMAN (J. Inst. Petrol. Tech., 1931, 17, 738—740).—The composition and probable origin of the ring are given. N. H. HARTSHORNE.

Soils from Argolis. E. BLANCK and F. GIESECKE (Chem. Erde, 1931, 6, 578—586).—Mechanical and chemical analyses (bulk analysis and analysis of the portion sol. in HCl) are given of yellow, brown, and red earths (terra rossa) from various localities in Argolis, Greece. Analyses are also given of the underlying limestone from which these soils were derived. L. J. SPENCER.

Reactions of horizons in tropical soils. A. J. W. HORNBY (Nature, 1932, 129, 58).—The p_H of soil samples from different depths of red soils of south-central Africa are discussed. In virgin soil max. acidity occurs for a depth of 2—3 feet in a region generally coincident with a tendency to pan formation. L. S. THEOBALD.

Organic Chemistry.

Synthesis of hydrocarbons at ordinary pressure from mixtures of carbon monoxide and hydrogen. M. G. LEVI, C. PADOVANI, and M. BUSI (Atti III Cong. Naz. Chim. pura appl., 1929, 718—729; Chem. Zentr., 1931, i, 3631—3632).—By the use at 257—285° of catalysts of Fe, Co, and Cu containing Mn or Cr oxides, reduced in N_2–H_2 mixtures or in N_2, yields of light liquid hydrocarbons up to 74·4 c.c. per cu. m. of gaseous mixture were obtained. A. A. ELDRIDGE.

Properties of conjugated compounds. XIV. Homogeneity of seven mono- and di-methylbutadienes and the influence of the position of alkyl substitution in these substances on refractivity. E. H. FARMER and F. L. WARREN (J.C.S., 1931, 3221—3235; cf. A., 1931, 1397).—The various methods of prep. of the methyl- and dimethylbutadienes are examined. B.-p. ranges, d, n, ε, and molar polarisation are recorded for the purest specimens and the optical data are discussed; the consts. vary most when the hydrocarbon can exist in geometrically isomeric forms. $\alpha\gamma$-, $\alpha\delta$-, and $\beta\gamma$-Dimethyl- and β-methyl-butadiene add quantitatively to maleic anhydride; $\alpha\beta$-dimethyl- and α-methyl-butadiene polymerise slightly and $\alpha\alpha$-dimethylbutadiene completely when treated with maleic anhydride. 3-*Methyl*- and 3 : 4-*dimethyl*-Δ^4-*tetrahydrophthalic anhydride* have m. p. 61° and 67°, respectively; the former with boiling H_2O gives the acid, m. p. 155°. R. S. CAHN.

Pyrogenic decomposition of a highly unsaturated hydrocarbon at high hydrogen pressure. R. ODA (J. Soc. Chem. Ind. Japan, 1931, 34, 386—388B).—Squalene, $C_{30}H_{50}$, b. p. 250—253°/1 mm., d^{15} 0·8601, I val. 370·35, is converted by H_2 at 450°/100 atm. (below which it is merely polymerised) into products of b. p. 39—260°; the lower fractions are olefines, the higher are terpenes, the I val. varying from 17·1 to 69·6. Fractions with much higher I val. (117—180 and 151—251) are obtained as by-products of polymerisation at 300° with and without H_2 pressure. C. HOLLINS.

Action of radon on unsaturated hydrocarbons. G. B. HEISIG (J. Amer. Chem. Soc., 1931, 53, 4460; cf. A., 1931, 1252).—Vinylacetylene condenses to a white solid which becomes orange as the exposure to the action of α-particles continues; about 11 mols. of the hydrocarbon polymerise per ion pair and practically no H_2 and CH_4 are evolved. C_3H_6 condenses to a light mobile liquid, and the amount of H_2 and CH_4 evolved is slightly lower than with C_2H_4; somewhat less than 3 mols. condense per ion pair. The energy relations show that condensation of the saturated hydrocarbons is endothermal, whilst that of the unsaturated compounds is exothermal; the latter condensations have a higher M/N ratio. C. J. WEST (*b*).

Thermal polymerisation of acetylene in presence of zinc chloride. A. V. LOZOVOJ (J. Gen. Chem. Russ., 1931, 1, 717—728).—Purified C_2H_2 was passed at 15 litres per hr. through a glass tube containing a 60—65-c.c. long layer of pumice + 5% $ZnCl_2$ at 420—430°; the gaseous products were 32% C_2H_2, 2% *iso*olefines, 10% *n*-olefines, 12% H_2, 41% CH_4, C_2H_6, etc. The unsaturated hydrocarbons identified were C_2H_4, propylene, Δ^a-propinine, allene, and butadiene. The liquid condensate (190 g. from 600 litres of C_2H_2) contained a small amount of olefines, C_6H_6, PhMe, and $C_{10}H_8$, but no paraffins or naphthenes. It is suggested that the propylene was formed from CH_4 and C_2H_2 and the butadiene from 2 mols. of C_2H_4; the formation of C_6H_6 takes place in two stages, the first being the combination of 2 mols. of C_2H_2 to ··CH⁚CH·CH⁚CH··, which can either form divinyl or unite with C_2H_2 to give C_6H_6. The propinine may be formed from propylene and then give rise to allene. G. A. R. KON.

[Friedel–Crafts syntheses in the aliphatic and hydroaromatic series.] J. VON BRAUN (Ber., 1931, 64, [*B*], 2869; cf. Hopff, this vol., 44).—Cases of occurrence of the Friedel–Crafts reaction with non-aromatic H have been recorded by the author (A., 1912, i, 435; 1928, 161). H. WREN.

Action of arylsulphonyl halides and esters on some metallic derivatives: syntheses in the acetylene series. R. TRUCHET (Ann. Chim., 1931, [x], 16, 309—419).—Arylsulphonyl chlorides and

CR⋮CNa react in Et_2O to give CR⋮CCl and Na arylsulphinates in 50—70% yield. Mg derivatives behave similarly, with smaller yields, but Ag and Cu derivatives of acetylenes do not react. The physical properties of *α-chloro-Δ^α-heptinene*, b. p. 141—142°, d^{18} 0·918, *-Δ^α-octinene*, b. p. 61—62°/17 mm. d^{20} 0·972, *-Δ^α-noninene*, b. p. 75—77°/15 mm., d^{20} 0·906, and -phenylacetylene, are described. The Cl does not react until the triple linking has been broken, differing from the Br- and I-derivatives. Hg salts cause the addition of H_2O (*hexoyl chloride*, b. p. 72—75°/20 mm.), I is added ($C_5H_4CI{\vdots}CICl$, b. p. 119—121°/2·5 mm.), NaOEt and KOEt give mixtures of the corresponding acids and esters, but $CH_2(CO_2Et)_2$ does not react. Na and Zn directly replace Cl either by the metal or by H, but do not dimerise the mol. Arylsulphonyl bromides and iodides behave similarly with CPh⋮CNa. The chlorides and RMgBr (R=Et, Me) give chiefly RCl and $ArSO_2{\cdot}MgBr$ with some sulphoxides and sulphides, but no sulphones (cf. Wedekind and Schenck, A., 1921, i, 664; Hepworth and Clapham, J.C.S., 1921, **119**, 1188), the latter being formed in secondary reactions. AcCl and acetylenes give chloroacetylenes and some CR⋮C·COMe. These reactions show that a metallic may be converted into a halogenoderivative by direct replacement, and the action is very general between many metallic derivatives and certain halogenated compounds RX in which the H or RH or ROH has acidic properties.

The reaction $R{\cdot}SO_3R'+CR''{\vdots}CNa \longrightarrow CR''{\vdots}CR'+R{\cdot}SO_3Na$ (R'=alkyl) has given in good yield the following: Δ^{β}-noninene; *Δ^{γ}-noninene*, b. p. 155—157°, d^{20} 0·763; *Δ^{γ}-decinene*, b. p. 175—176°, d^{21} 0·765; *Δ^{δ}-decinene*, b. p. 74—75°/19 mm., d^{17} 0·772; phenyl-methyl-, -ethyl-, *-propyl-*, b. p. 213—215°, d^{18} 0·911, *-butyl-*, b. p. 114—115°/14 mm., d^{17} 0·899, *butylamyl-*, b. p. 195—197°, d^{20} 0·785, and *diamyl-acetylene*, b. p. 103—104°/14 mm., d^{18} 0·790. The physical properties, including the parachor and absorption spectra, of these are given. F. R. Shaw.

Fluorination of compounds of carbon (benzene and carbon tetrachloride with iodine pentafluoride, and carbon tetrachloride with fluorine). O. Ruff and R. Keim (Z. anorg. Chem., 1931, **201**, 245—258; cf. A., 1930, 1387).—IF_5 and C_6H_6 interact at room temp. to give HF, PhI, and charred material. Under similar conditions CCl_4 gives CCl_3F with Cl_2, ICl, and ICl_3. CCl_4 at its b. p. reacts with F_2 to give a mixture of CCl_3F, CCl_2F_2, *chlorotrifluoromethane*, and CF_4. Addition of I, As, Sb, W, or CoF_3 to the reaction mixture is desirable to avoid explosions. The following data are given: CCl_3F, b. p. 24·1°, d_4^{-78} 1·72; CCl_2F_2, b. p. −28°, d_4^{-85} 1·67; $CClF_3$, b. p. −80°, d_4^{-130} 1·726. F. L. Usher.

Preparation of chloropicrin. E. O. G. Frahm (Rec. trav. chim., 1931, **50**, 1125—1126).—A modification of the method of B.P. 142,878 (A., 1918, i, 521). $CCl_3{\cdot}NO_2$ is obtained in 95—98% yield by passage of Cl_2 at 0° into an aq. solution of Ca picrate containing $Ca(OH)_2$ in suspension. H. A. Piggott.

New hypnotic, ethyl-β-ethylbutylbarbituric acid, and some derivatives of β-ethylbutyl alcohol. E. Fourneau and J. Matti (J. Pharm. Chim., 1931, [viii], **14**, 513—522).—β-Ethylbutyl alcohol with Ac_2O and 3 drops of H_2SO_4 gives the *acetate*, b. p. 63°/20 mm., with 48% HBr and H_2SO_4 the *bromide* (I), b. p. 143—144°/762 mm., and with 45% HCl and a little H_2SO_4 the *chloride*, b. p. 125—127°. (I) with NaI in $COMe_2$ gives the *iodide*, b. p. 160°/763 mm., and with Et sodiomalonate *Et_2 (β-ethylbutyl)malonate*, b. p. 140°/16 mm., which with NaOEt and EtBr yields *Et_2 ethyl-β-ethylbutylmalonate* (II), b. p. 158°/27 mm. (II) with carbamide and NaOEt affords *ethyl-β-ethylbutylbarbituric acid*, m. p. 125°, and an oil, whilst hydrolysis and distillation of the acid gives *αγ-diethylhexoic acid*, b. p. 145°/24 mm.; the *Et* ester, b. p. 106—107°/25 mm., of the latter acid with Na and dry EtOH gives *αγ-diethylhexyl alcohol*, b. p. 123—125°/43 mm. (*acetate*, b. p. 116—117°/25 mm.). Treatment of the Grignard reagent from (I) with *iso*butaldehyde gives *β-methyl-ε-ethylheptan-γ-ol*, b. p. 92°/28 mm. (*acetate*, b. p. 94—96°/24 mm.), together with other products, and with chloroacetone affords the chlorohydrin, which with $NHMe_2$ in C_6H_6 at 120—130° yields *methyl-(β-ethylbutyl)(dimethylaminoethyl)carbinol*, b. p. 115—116°/27 mm. The hydrochloride of the benzoate of the last-named compound has strong anæsthetic action on the tip of the tongue. R. S. Cahn.

Attempts to resolve r-amyl alcohol (β-methylbutanol). F. von Falkenhausen (Biochem. Z., 1931, **242**, 472—481).—Attempts to resolve the alcohol by way of the brucine and strychnine monoamyl phosphates, morphine monoamyl 3-nitrophthalate, the H tartrate and the α-bromo-*d*-camphor-π-sulphonate of α-amino-γ-methylbutane, the condensation product of the latter with hydroxymethylenecamphor, and in other similar ways were unsuccessful possibly because mixed crystals are produced. W. McCartney.

Synthesis of pure optically active amyl alcohol. F. von Falkenhausen and C. Neuberg (Biochem. Z., 1931, **242**, 482—486; cf. A., 1929, 907).—By repeated recrystallisation of the product obtained from β-acetobromoglucose and *sec.*-butylcarbinol in the manner previously described pure dl-*amyl*-β-d-*tetra-acetylglucoside*, m. p. 101—102°, is obtained. On hydrolysis this compound yields pure *d*-amyl alcohol, b. p. 128°, $[\alpha]_D^{20}$ −5·88°. β-dl-*Amyl*-d-*glucoside* has m. p. 89—90°. W. McCartney.

Synthesis and characterisation of βδ-dimethylpentan-α-ol. T. Chu and C. S. Marvel (J. Amer. Chem. Soc., 1931, **53**, 4449).—$MgBu^{\beta}Br$ and MeCHO give 49% of $CH_2Pr^{\beta}{\cdot}CHMe{\cdot}OH$, b. p. 129—131°; the bromide, b. p. 130—132°, of this with Mg and CH_2O give 30% of *βδ-dimethylpentan-α-ol*, b. p. 65—67°/18 mm., 160—162° (3-*nitrophthalate*, m. p. 154—155°). C. J. West (*b*).

Configurative relationships of carbinols of the *iso*butyl series and of benzylethylcarbinol to the simple aliphatic carbinols. P. A. Levene and A. Walti (J. Biol. Chem., 1931, **94**, 367—372).—The conclusion previously reached (A., 1931, 599) that configuratively related *n*- and *iso*-butylcarbinols rotate in the same direction is confirmed by the prep. of l-*methyl*iso*butylcarbinol*, b. p. 65—66°/60 mm. (*α-naphthylurethane*, m. p. 86—89°, $[\alpha]_D^{23}$ −3·72° in EtOH), from *d*-propylene oxide and $MgPr^{\beta}Br$, and of l-*ethyl*iso*butylcarbinol*, b. p. 63—64°/19 mm. (α-*naphthylurethane*, m. p. 77—79°, $[\alpha]_D^{24}$ −1·5° in EtOH), and l-*ethylbutylcarbinol*, b. p. 66°/18 mm., α_D^{23} −0·9° (α-*naphthylurethane*, m. p. 74—75·5°), from *d*-α-butylene oxide (I) and $MgPr^{\beta}Br$ and MgPrBr, respectively. (I) is prepared from *l*-β-hydroxybutyl bromide and conc. NaOH at 90°, and is converted by aq. HBr into a l-*bromohydrin*, b. p. 70—71°/23 mm. l-*Benzylethylcarbinol*, b. p. 126°/27 mm. (α-*naphthylurethane*, m. p. 116—119°), from (I) and MgPhBr, is configuratively related to ethyl-*n*-alkylcarbinols rotating in the same direction (cf. A., 1930, 1178). H. BURTON.

Phytochemical reductions. Configurations of glycols obtained by reduction with fermenting yeast. P. A. LEVENE and A. WALTI (J. Biol. Chem., 1931, **94**, 361—366).—α-Hydroxy-aldehydes are not reduced so readily by fermenting yeast as the β-keto-alcohols, $R{\cdot}CO{\cdot}CH_2{\cdot}OH$ (A., 1927, 337). When reduction does occur, optically active glycols of the same configuration as those from the keto-alcohols are produced. Similar reduction of the γ-keto-alcohols, $R{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, gives optically active glycols of opposite configuration. The optically active glycols result from true asymmetric reductions. *Pentane*-αβ-*diol*, b. p. 98—102°/13 mm., $[\alpha]_D^{20}$ +3·75° in EtOH (*diphenylurethane*, m. p. 97—98°), *hexane*-αβ-*diol*, b. p. 111°/12 mm., $[\alpha]_D^{22}$ +0·58° in EtOH, and l-*butane*-αγ-*diol*, b. p. 107—110°/23 mm., $[\alpha]_D^{18}$ −18·8° in EtOH (*diphenylurethane*, m. p. 127—128°), are obtained from α-hydroxy-valeraldehyde and -hexaldehyde, and β-acetylethyl alcohol, respectively. *d*-β-Hydroxybutyric acid, obtained by reduction of acetoacetic acid (Friedmann, A., 1931, 1091), has the same configuration as the glycol formed from aldol. H. BURTON.

Compounds of bivalent carbon. IV. Sodiumoxyethoxymethylene. H. SCHEIBLER [with E. BAUMANN] (Ber., 1931, **64**, [*B*], 2914—2916; cf. A., 1927, 338; Adickes, A., 1931, 196).—The action of CO at 20°/80 atm. on NaOEt free from EtOH causes increase in wt. corresponding with production of about 30% of sodiumoxyethoxymethylene. The product is hydrolysed by H_2O to HCO_2Na and EtOH. H. WREN.

Ethyl ethers of α-glycols. II. D. BADRAN (Bull. Soc. chim., 1931, [iv], **49**, 1551—1555).—When dehydrated with P_2O_5 in presence of pyridine at 140°, the Et ethers of α-glycols, $OH{\cdot}CR_2{\cdot}CHR'{\cdot}OH$, are converted into the olefinic Et ethers, $CR_2{:}CR'{\cdot}OEt$, from which by hydrolysis with 20% H_2SO_4 the same ketones, $CHR_2{\cdot}COR'$, are obtained as are prepared in 40—50% yield by the action of HCO_2H, $H_2C_2O_4$, or 20% H_2SO_4 on the original α-glycol ethers. Thus γ-ethoxy-δ-propylheptan-δ-ol yields 90% of γ-*ethoxy*-δ-*propyl*-Δ^{γ}-*heptene*, b. p. 108—109°/17 mm., giving with Br (2 atoms) in CS_2 a dibromide which yielded no glycol with aq. $Ba(OH)_2$, did not react with $NPhMe_2$, and on distillation yielded a small fraction, b. p. 115—138°/15 mm. With O_3 in $CHCl_3$, γ-ethoxy-δ-propyl-Δ^{γ}-heptene gives the corresponding *ethylene oxide*, b. p. 120—121°/19 mm., hydrolysed by 10% H_2SO_4 to δ-hydroxy-δ-propylheptan-γ-one, b. p. 102—104°/24 mm. α-Ethoxy-α-phenyl-β-ethyl-Δ^{α}-butene, b. p. 134—135°/15 mm. (yield, 90%), similarly gives a Br-derivative yielding a fraction, b. p. 138—142°/18 mm. β-Ethoxy-αα-diphenyl-Δ^{α}-propene (90%), b. p. 141—147°/6·5 mm.; γ-*ethoxy*-δ-*butyl*-Δ^{γ}-*octene* (94%), b. p. 124—127°/16 mm.; and α-*ethoxy*-α-*phenyl*-β-*butyl*-Δ^{α}-*hexene*, b. p. 165—167°/14·5 mm., are described. R. BRIGHTMAN.

Glycerophosphomolybdates. P. FLEURY (Compt. rend., 1931, **193**, 1350—1352).—The optical activity of aq. solutions of NH_4 molybdomalate decreases following addition of Na_2 α- and β-glycerophosphates or of Na_2HPO_4 (cf. A., 1926, 778). Solutions of $(NH_4)_2MoO_4$ to which NaH_2PO_4 or Na α- or β-glycerophosphate is added become progressively alkaline until a const. val. is attained. Treatment with EtOH of appropriate solutions of β-glycerophosphate and $MoO_3,2H_2O$ results in the separation of the cryst. *salts*, $2{\cdot}5MoO_3,\beta(C_3H_7O_2),Na_2PO_4,4H_2O$ and $2{\cdot}5MoO_3,\beta(C_3H_7O_2),K_2PO_4,2{\cdot}5H_2O$. F. O. HOWITT.

***iso*Propylideneglucose 3-phosphate and its triphenylmethyl ester.** K. JOSEPHSON (Svensk Kem. Tidskr., 1931, **43**, 242—244; cf. A., 1930, 1166).—The suggested constitution of *iso*propylideneglucose phosphate has now been confirmed by determination of the amount of $COMe_2$ liberated by the action of mineral acids and by the prep. of its CPh_3 derivative, m. p. about 130°, $[\alpha]_{\text{Hg yellow}}^{20}$ −24·7° in $COMe_2$. H. F. HARWOOD.

Reactivity of the mercaptido-group. I. N. HELLSTRÖM.—See this vol., 26.

Bismuth derivative of sodium β-hydroxy-γ-thiolpropanesulphonate. A. LEULIER and M. JUVIN.—See this vol., 192.

Metallic derivatives of the enolic forms of monocarbonyl compounds. XIII. Course of the reaction of the Claisen–Darzens glycidic ester synthesis. H. SCHEIBLER and P. S. TUTUNDZITSCH (Ber., 1931, **64**, [*B*], 2916—2920).—Condensation of $CH_2Cl{\cdot}CO_2Et$ with PhCHO in presence of NaOEt and Et_2O affords Et phenylglycidate (converted into phenylglycidic acid and thence into $CH_2Ph{\cdot}CHO$) and a little α-chlorocinnamic acid. Other condensing agents give similar results and hence, contrary to Rutovski and Dajev (A., 1931, 604), the reaction is capable of a uniform interpretation involving the intermediate production of the ester enolate $CHCl{:}C(OEt){\cdot}ONa$. Similarly, furfuraldehyde, NaOEt, and $CH_2Cl{\cdot}CO_2Et$ afford *Na furylglycidate*, converted by conc. aq. tartaric acid in presence of Et_2O into *furylacetaldehyde*, a mobile oil which readily polymerises. $CO(CH_2Ph)_2$ is transformed into *dibenzylglycidic acid*, slowly converted by dil. H_2SO_4 into β-*phenyl*-α-*benzylpropaldehyde*, b. p. 140—150°/1 mm., which does not react with NH_3, $NaHSO_3$, $NHPh{\cdot}NH_2$, $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, or NH_2OH, but gives an *azine*, m. p. 79°. H. WREN.

Reaction of anhydrous sodium acetate with alkyl trichloromethyl carbonates. N. N. MELNIKOV and (MLLE.) E. A. SIDOROVA (J. Gen. Chem. Russ., 1931, **1**, 740—742).—Ph, *p*-tolyl, and *iso*amyl CCl_3 carbonates with NaOAc yield Ac_2O and the corresponding alkyl acetate. It is suggested that the esters first decompose into $COCl_2$, which gives rise to Ac_2O, and an alkyl chloroformate, which gives CO_2 and the alkyl acetate. Hexachloromethyl carbonate (triphosgene) gives Ac_2O only. $CPhCl_3$ and BzOH give BzOPh, CO_2, and HCl. G. A. R. Kon.

Resolution of racemates by formation of complex compounds. H. Sobotka (Naturwiss., 1931, **19**, 595—596).—The formation of complex compounds with optically active substances has been studied, and the use of the method for resolution is described. Deoxycholic acid forms mol. compounds by combination with substances in the mol. proportions 1 : 1, 1 : 2, 1 : 3, 1 : 4, 1 : 6, etc. From a solution of pure deoxycholic acid in β-methylbutyric acid there crystallised β-methylbutyric–cholic acid, with co-ordination no. 2. The β-methylbutyric acid in this mol. compound was not completely racemic, but contained an excess of the *l*-acid. By distillation of the mother-liquor the *d*-form was obtained. An analogous effect is obtained with camphor. The method is also useful for the investigation of *cis–trans* isomerism.

A. J. Mee.

Dehydrogeranic acid. R. S. Cahn, A. R. Penfold, and J. L. Simonsen (J.C.S., 1931, 3134—3142).—The oil obtained in 6·7% yield by steam-distillation of the wood of *Callitropsis araucarioides* is hydrolysed by 0·5*N*-KOH, yielding some *dehydrogeranic acid* (I), $C_{10}H_{14}O_2$, decomp. 185—186° (sinters at 183°), which is optically inactive and decomposes (oxidises) when kept. (I) is unsaturated ($KMnO_4$, Br), could not be condensed with maleic anhydride, is oxidised by alkaline $KMnO_4$ to $COMe_2$, HCO_2H, AcOH, and $H_2C_2O_4$, and is reduced catalytically (Pd–norite) (with absorption of 6H) to *dl*-tetrahydrogeranic acid (p-*toluidide*, m. p. 81—82°), also prepared by similar reduction of geranic acid. The absorption spectrum in EtOH favours the structure $CMe_2{:}CH\cdot CH{:}CH\cdot CMe{:}CH\cdot CO_2H$ for (I). The results of a preliminary *X*-ray investigation of (I) are given.

H. Burton.

Configurative relationship of α-hydroxyheptoic acid to other α-hydroxy-acids. P. A. Levene and A. Walti (J. Biol. Chem., 1931, **94**, 593—598).—Amylvinylcarbinol is resolved through the H phthalate by strychnine into *d*- and l-*forms*, b. p. 78°/19 mm. The *d*-form is reduced catalytically (PtO_2) to l-*ethylamylcarbinol*, b. p. 82°/24 mm., $[\alpha]_D^{17}$ —7·4° in EtOH (*α-naphthylurethane*, m. p. 79—80°). *d*-α-Hydroxyheptaldehyde (this vol., 145) is reduced with Na–Hg in 80% EtOH (kept slightly alkaline by addition of 10% H_2SO_4) to d-*heptane*-αβ-*diol*, b. p. 90°/about 1 mm., $[\alpha]_D^{25}$ +11·92° in EtOH (*diphenylurethane*, m. p. 109°), and is oxidised by Goebel's method (A., 1927, 647) to *l*-α-hydroxyheptoic acid, $[\alpha]_D^{25}$ $-1{\cdot}0\pm0{\cdot}005°$ in aq. EtOH (*Ba* salt; Na salt, $[\alpha]_D^{25}$ $+7{\cdot}5\pm0{\cdot}2°$ in H_2O). The same relationship of structure to rotation holds in the case of α-hydroxyheptoic acid as in the other α-hydroxy-acids examined (A., 1928, 1353). H. Burton.

Reactions in the determination of iodine value. M. Settimj (Annali Chim. Appl., 1931, **21**, 507—525).—Determinations with erucic acid by Hübl's method show that the acidity generated during the process is to be attributed to the re-establishing of the ethylenic linking and that the iodoxy-derivative produced by HIO takes up HCl so that the end product consists mainly of a chloroiodo-derivative.

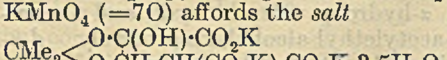
O. F. Lubatti.

Determination of citric acid by Kogan's method. B. Romani (Annali Chim. Appl., 1931, **21**, 496—500).—This method (A., 1930, 743) is unsatisfactory because the amount of $COMe_2$ formed by the oxidation of citric acid with $KMnO_4$ is not theoretical, but changes with small variations of the conditions of the oxidation, other compounds, such as aconitic acid and probably acraldehyde, being formed as well. Secondly, the amount of $COMe_2$ obtained in the reaction cannot be completely distilled.

O. F. Lubatti.

Mechanism of saccharic acid formation. B. H. Nicolet (J. Amer. Chem. Soc., 1931, **53**, 4458).—The action of alkali on $OMe\cdot CHPh\cdot CH(OH)\cdot COPh$ gives αβ-diphenyl-lactic acid in good yield; the initial reaction is considered to be of the type of an "aldol dehydration," and its occurrence seems to require the revision of Nef's interpretation of the mechanism by which sugars form saccharic acids. This will be discussed later. C. J. West (*b*).

Model experiments based on the theory of alcoholic fermentation. V. Oxidation of α-ketogluconic acid and β-di*iso*propylidenefructose. H. Ohle and F. Garcia y Gonzalez (Ber., 1931, **64**, [*B*], 2804—2809; cf. A., 1931, 1039).—Oxidation of K α-ketodi*iso*propylidenegluconate in H_2O at 100° with $KMnO_4$ (=7O) affords the *salt*



$$CMe_2{<}\begin{matrix}O\cdot C(OH)\cdot CO_2K\\ O\cdot CH\cdot CH(CO_2K)\cdot CO_2K,3\cdot5H_2O,\end{matrix}$$

$[\alpha]_D^{20}$ + 10·39° in H_2O (also $+H_2O$) (basic *Pb* salt), quantitatively hydrolysed by dil. mineral acids to CO_2, glycollic acid, and glycollaldehyde or their transformation products. β-Di*iso*propylidenefructose is oxidised by $KMnO_4$ in alkaline solution almost quantitatively to α-ketodi*iso*propylidenegluconic acid, but this is not produced in initially neutral solution, in which *K α-keto*-βγ-iso*propylidenedioxyglutarate*, $[\alpha]_D^{20}$ +32·80° in H_2O (corresponding *basic Pb* salt), is formed; admixture with K α-keto-β-hydroxysuccinate is not excluded. The salt is hydrolysed by dil. mineral acids to CO_2, and glyceraldehyde or methylglyoxal.

H. Wren.

Composition of copper xanthate. M. P. Matuszak (J. Amer. Chem. Soc., 1931, **53**, 4451—4452).—The Cu content of the ppt. obtained by adding excess of $CuSO_4$ to fresh solutions of K xanthate indicates that the ppt. is undoubtedly the Cu˙ salt, $CuS\cdot CS\cdot OEt$.

C. J. West (*b*).

Acceleration of aldol condensation by amino-acids. F. G. Fischer and A. Marschall (Ber., 1931, **64**, [*B*], 2825—2827).—NH_2-acids accelerate the aldol condensation in solutions buffered so as to be nearly neutral. MeCHO in presence of phosphate buffer and alanine yields mainly aldol and crotonaldehyde or more highly condensed products including hexadienal. Borate buffer may be used. The activity of the monoamino-acids is very weak at p_H 6, most marked between p_H 7 and 8; in more strongly alkaline solution the condensing action of OH ions is disturbing. Acceleration is observed with but- and crotonaldehyde and γ-methyl-Δ^{β}-butenal; it is less marked with CH_2O, but obvious at p_H 8—9. Leucyl-leucine and albumin are feeble accelerators. Primary and secondary aliphatic amines are active, but hippuric acid is ineffective. H. Wren.

Colour reaction of formaldehyde and ketones with sodium nitroprusside and hydroxylamine. P. Pratesi (Giorn. Chim. Ind. Appl., 1931, **13**, 513).—Na nitroprusside solution (not too dil.) is treated with NH_2OH salt crystals and a few drops of 40% CH_2O solution. On adding about 2*N*-NaOH, a transient yellow coloration is first produced, and then a stable, intense violet-red coloration. Aliphatic ketones give a similar, but unstable, coloration. T. H. Pope.

Preparation and determination of acraldehyde. E. V. Zappi and R. A. Labriola (Anal. Asoc. Quím. Argentina, 1930, **18**, 243—246).—Slight modifications in the prep. of acraldehyde (Org. Syntheses, 1926, 6, 1) are described. Acraldehyde may be determined by treatment with excess of $NaHSO_3$ and back-titration with I (Ivanov, A., 1911, ii, 419) or, less satisfactorily, by treatment with Br in CCl_4 or $CHCl_3$ and titration of excess of Br. R. K. Callow.

Polymerisation and condensation. VII. Polymerisation of α-hydroxy-aldehydes. P. A. Levene and A. Walti (J. Biol. Chem., 1931, **94**, 353—360).—α-Hydroxy-propaldehyde, -butaldehyde, and -valeraldehyde (dimeride, m. p. 145°), prepared by reduction of the ozonides of methyl-, ethyl-, and propyl-vinylcarbinols, respectively, with Zn dust and AcOH, are mobile liquids when freshly distilled; they polymerise readily at room temp. to viscous liquids which gradually deposit cryst. (dimeric) material. α-Hydroxyhexaldehyde (I), b. p. about 60°/1—2 mm. (ultra-violet absorption spectrum given), prepared similarly from Δ^{β}-octen-δ-ol, affords a *dimeride*, m. p. 150°, which when distilled at 0·5 mm. pressure regenerates (I). The rotations of d-, b. p. 70—75°/about 3 mm., and l-, b. p. 109—111°/25 mm., *-α-hydroxy-heptaldehydes*, prepared from *l*- and *d*-amylvinylcarbinols, respectively, increase considerably during the process of polymerisation. H. Burton.

Preparation of keten. E. Peytral (Compt. rend., 1931, **193**, 1199—1200).—A small proportion of keten is obtained by passing vapours of Ac_2O through a Pt tube at 800°; removal of AcOH and unchanged Ac_2O by cooling to 0° gives a gas containing only 0·5—1% of impurities, mainly CO and C_2H_4. H. A. Piggott.

Reactions of carbon disulphide. II. Reaction with acetone. E. Wertheim (J. Amer. Chem. Soc., 1931, **53**, 4037—4045; cf. A., 1926, 497).—Repetition of the work of Apitzsch (A., 1904, i, 510; 1905, i, 810; 1909, i, 46), in which $COMe_2$ was treated with solid KOH and CS_2, gave evidence of the production of an acidic S compound, which could not be isolated. The reaction between CS_2, $COMe_2$, and Na is complex; the H_2 liberated is 98·2% of that required by the equation $CH_2{:}CMe{\cdot}OH+CS_2+Na \longrightarrow CH_2{:}CMe{\cdot}OCS_2Na+H$. The part insol. in Et_2O–$COMe_2$ consists largely of Na trithionate (obtained in about 50% yield), and the Et_2O–$COMe_2$ filtrate with BzCl gives the *Bz* derivative, m. p. 155—156° (*Ag* salt), of acetonebiscarbithioic acid; with NaOMe this yields the *Me ether*, m. p. 150—151°, of the enol form of the acid. The filtrate also contained a little mesityl oxide. When the filtrate was acidified, a salmon compound, probably *acetone-αγ-biscarbithioic acid*, m.p. 84—85° (*Ag* salt), which has a disagreeable, fæcal odour, was pptd.; this loses H_2S when suspended in H_2O or when heated, giving *αγ-bisthiocarbonylacetone*, amorphous, decomp. about 200°; on heating in air, SO_2 is formed. The mixture of Na salts in the above reaction and MeI in MeOH give Me trithiocarbonate, also obtained similarly from $COMe_2$, CS_2, and solid KOH, and from the NH_4 salt of the acid and MeI. *s*-Methyl *iso*propyl xanthate has b. p. 65—68°/5 mm., 175—179°/729 mm. C. J. West (*b*).

Photosynthesis of carbohydrates *in vitro*. J. Bell.—See this vol., 29.

Structure of oses and diholosides. M. Bridel (Bull. Soc. Chim. biol., 1931, **13**, 1015—1155).—A lecture.

Characterisation of aldehydic and ketonic sugars by oxidation with bromine. F. Zanelli (Giorn. Chim. Ind. Appl., 1931, **13**, 514—515).—In aq. solution containing much AcOH, keto-sugars are not oxidised to an appreciable extent by Br (B., 1909, 919), whereas with aldo-sugars the CHO group undergoes complete oxidation. Exact conditions for the test are given. T. H. Pope.

Action of certain moulds on solutions of aldoses. II. A. Angeletti and C. F. Cerutti (Annali Chim. Appl., 1931, **21**, 491—496).—Cultures of *Penicillium luteum purpurogenum* (strain 2A.3) on solutions of *l*-arabinose do not show any acid products after 20 days' incubation. In solutions of *d*-xylose, under the same conditions, small amounts of an acid (probably *d*-xylonic acid) are formed. Thus this fungus is able to oxidise to acid products, *d*-glucose, *d*-mannose (A., 1930, 1620), and *d*-xylose, but not *d*-galactose and *d*-arabinose. The behaviour is attributed to the arrangement of the atoms or at. groups around the C atoms 3 and 4 in the chain. O. F. Lubatti.

Molisch's reaction. H. Bredereck (Ber., 1931, **64**, [*B*], 2856—2859).—α-Naphthol condenses with furfuraldehyde in presence of 10% NaOH to 2-*furyl-di*-4-*hydroxy*-1-*naphthylmethane* (*Ac_2* and *Bz_2* derivatives), which when covered with conc. H_2SO_4 gives a dark red to bluish-violet solution closely similar to that obtained in the Molisch and von Udransky reaction. Arabinose when treated according to Molisch and then acetylated appears to yield the same Ac_2 derivative. In the case of pentoses, therefore, the Molisch reaction appears to depend on primary conversion of the sugar into furfuraldehyde. H. Wren.

Reactivity of the methylated sugars. V. Action of dilute alkali on trimethyl-*l*-arabinose. H. T. Neher [with W. L. Lewis] (J. Amer. Chem. Soc., 1931, **53**, 4411—4423; cf. A., 1931, 1037).—The blocking effect of the Me group on enolisation has been previously demonstrated; these conceptions are now extended to trimethyl-*l*-arabinose. The sp.

rotation of *l*-arabinose in saturated aq. $Ca(OH)_2$ at 35° falls from +100° to +62·6° in 195 hr., and shows no further change for 2 months. The aldose content (by I titration) falls from 99·7 to 84·9%, thus showing no intermediate high I-absorbing compound, but indicating the formation of ketose. Trimethyl-*l*-arabinose, m. p. 81—82°, obtained in 80% yield by careful hydrolysis of its α-methyl derivative (m. p. 46—46·5°) with 4% HCl, is probably a mixture of the α- and β-forms, since the initial rotation varies with the conditions of crystallisation; all the specimens mutarotate (to a const. val. of $[\alpha]_D^{25}$ +158°); the lowest val. observed in $CHCl_3$ was $[\alpha]_D^{20}$ +16·4°, believed to be nearly that of the pure α-form. With aq. $Ca(OH)_2$ at 35° optical equilibrium was attained in 164 hr. with $[\alpha]_D^{35}$ +98°; the % of apparent aldose (by I titration) gradually rose from 100 to 150—155%, as with the other methylated sugars studied. The high I absorption is probably due to the presence of a relatively stable intermediate methylated ene-diol. Treatment of the enolised solution with acid brought the I val. back to 100% aldose, but with more difficulty than with the methylated hexoses. An equilibrated solution of trimethylarabinose (neutral or slightly alkaline) gave no test for furfuraldehyde; distillation of this solution in N_2 gave 0·30 mol. of MeOH (per mol. of sugar) and a trace of furfuraldehyde (≡0·07% of the sugar). Acidification of this solution caused the apparent aldose val. to fall to nearly 100% and the amount of furfuraldehyde present was equiv. to decomp. of 16·7% of the sugar originally present. From the de-enolised and neutralised solution, there was obtained 0·54 mol. of MeOH. The total MeOH obtained (0·84 mol.) would account for a min. val. of 28% of the sugar originally present, assuming that each mol. loses 3 OMe groups. The sugar obtained from the solution gave an aldose val. of 99·3%, $[\alpha]_D^{26}$ +138°, amounted to 64·6% of the original sugar, and contained 48·3% of trimethylarabinose. It is believed that the immediate source of furfuraldehyde is the high I-absorbing form (probably the enol) of the methylated sugar, which is produced by the action of the alkali. *l*-Arabinose yields no furfuraldehyde with acid of the concn. used. Trimethyl-*l*-arabinose is not the direct source of furfuraldehyde, as this is not obtained using 6*N*-acid (after 8 hr.) and only in small amounts with 12*N*-acid. A mechanism for the formation of furfuraldehyde is proposed. C. J. WEST (*b*).

Aldehydo-*d*-xylose tetra-acetate and the mercaptals of xylose and maltose. M. L. WOLFROM, M. R. NEWLIN, and E. E. STAHLY (J. Amer. Chem. Soc., 1931, **53**, 4379—4383).—The reaction product from xylose, EtSH, and conc. HCl is freed from HCl with $PbCO_3$ and Ag_2CO_3, and the resulting syrup acetylated with Ac_2O in pyridine; the *tetra-acetate* (I), m. p. 46—48° (corr.), $[\alpha]_D^{23}$ +13° in $CHCl_3$, of d-*xylose ethylmercaptal* (II), m. p. 63—65°, $[\alpha]_D^{25}$ −30·8° in $CHCl_3$, is thereby obtained. (II) may be obtained from the above-mentioned syrup (by seeding) in 70% yields. (I) treated with $CdCO_3$ and $HgCl_2$ in $COMe_2$ gives *aldehydo*-d-*xylose tetra-acetate* (III), m. p. 87—89°, $[\alpha]_D^{26}$ −15·9° in $CHCl_3$; in MeOH the initial rotation of +3·7° changes slowly to +2·5° in 2 days. A cold aq. solution of (III) gives a faint pink colour with Schiff's reagent in 1·5 min.; it reacts immediately with hot Fehling's solution. Maltose and EtSH, followed by acetylation, give *maltose ethylmercaptal octa-acetate*, m. p. 122—122·5°, $[\alpha]_D^{25}$ +87·5° in $CHCl_3$. C. J. WEST (*b*).

Novel modification of methyl-*d*-xyloside. R. C. HOCKETT and C. S. HUDSON (J. Amer. Chem. Soc., 1931, **53**, 4454—4455).—Condensation of *d*-xylose with MeOH gives β-methyl-*d*-xyloside and a mol. compound, α-*methyl*-d-*xyloside*–β-*methyl*-d-*xyloside* (7 : 2), m. p. 89—91°, $[\alpha]_D^{21}$ +104·4° in H_2O. Acetylation in the cold gives a mixture of the tetra-acetates of the known α- and β-methylxylosides, the former predominating; the rate of hydrolysis by 0·05*N*-HCl is $k=0{\cdot}00121\pm2\times10^{-5}$ at 99°. An actual mixture of the ordinary α- and β-forms in the ratio of 7 : 2 has $[\alpha]_D$ +105·4° and $k=0{\cdot}00125\pm3\times10^{-5}$. The mol. compound can be separated (with difficulty) into its components by crystallisation from AcOEt. C. J. WEST (*b*).

Reaction of methylpentosides and of α-methylmannoside with triphenylmethyl chloride. R. C. HOCKETT and C. S. HUDSON (J. Amer. Chem. Soc., 1931, **53**, 4456—4457).—α- and β-Methyl-*d*-xyloside, α-methyl-*d*-lyxoside, and β-methyl-*d*-arabinoside react with CPh_3Cl in pyridine, as shown by polarimetric changes in the *l*-direction; reaction is complete in 100—360 hr., and 45—80% of the original sugar reacts. Cryst. products have not been isolated. These results show that CPh_3Cl is not sp. in action towards primary OH groups, or that none of these methylpentosides has a 1 : 5-ring, or that ring shifts can occur. α-Methyl-*d*-mannoside has yielded a cryst. condensation product, which is being studied. C. J. WEST (*b*).

Identity of quinovose with *d*-glucomethylose (*iso*rhodeose). E. VOTOČEK and F. RAC (Chem. Listy, 1931, 25, 465—468).—The above sugars are identical. R. TRUSZKOWSKI.

Optical rotation of rhamnose- and mannose-phenylhydrazones. C. L. BUTLER and L. H. CRETCHER (J. Amer. Chem. Soc., 1931, **53**, 4358—4363).—Mannosephenylhydrazone, m. p. 199—200°, has $[\alpha]_D$ +26·3° in pyridine, decreasing to about +6° in 7 hr. and then slowly increasing to +33·8° (67 hr.). In EtOH–pyridine (1 : 1) the initial val. of +27·3° dropped to −2·6°, and then increased slowly to a const. val. slightly higher than the initial rotation; the rate of change was different in 2 experiments. The sp. rotation of rhamnosephenylhydrazone, m. p. 158—159°, in H_2O changes from +57·1° (initial) to +44·3° in 41 hr. In EtOH–pyridine (1 : 1) the initial val. was somewhat below −24°; this rapidly increased to a max. of +16°, and then slowly decreased and became const. at −35°, −100°, and −67·3° (in 3 experiments); the rate of change increased with the age of the sample. No explanation of this behaviour can be offered at present. C. J. WEST (*b*).

Optical rotation of the isomeric nitrophenylhydrazones of rhamnose and mannose. C. L. BUTLER and L. H. CRETCHER (J. Amer. Chem. Soc., 1931, **53**, 4363—4367).—*Rhamnose*-o-*nitrophenylhydr-*

azone, m. p. 152—153°, had $[\alpha]_D$ −37·5° $\longrightarrow$ −33·5° (24 hr.) in EtOH–pyridine (1 : 1); the m-*isomeride*, m. p. 158—159°, changed from −21° to +18·3° in 141·5 hr.; the *p*-isomeride, m. p. 191—192°, changed from −50·3° to −8·5° in 144 hr. *Mannose*-o-*nitrophenylhydrazone*, m. p. 172—173°, $[\alpha]_D$ +52°, and the *p*-isomeride, m. p. 202—203°, $[\alpha]_D$ +56°, showed no mutarotation; the m-*isomeride*, m. p. 162—163°, changed from +26·5° to −8·3° in 144 hr. These vals. do not agree with those which might be expected on the basis of rules found to hold for other classes of optically active position isomerides (cf. Cohen, J.C.S., 1910, **97**, 1732; 1911, **99**, 1058; Frankland, *ibid.*, 1912, **101**, 654), but the variations appear less erratic than the variations in the rotations previously recorded. C. J. WEST (*b*).

Syntheses in the sugar group. III. 1-Phenylglucosone, 1 : 1-diphenylfructose, and 1 : 1-dibenzylfructose. H. OHLE and I. BLELL (Annalen, 1931, **492**, 1—21; cf. A., 1930, 1274).—α-Ketodi*iso*propylidenegluconic acid (I) (1 mol.) and MgPhBr (6 mols.) in Et_2O–C_6H_6 give 1-*phenyl*-2 : 3 : 4 : 5-*di*iso*propylideneglucosone* (II), b. p. 166°/0·3 mm., m. p. 134°, $[\alpha]_D^{18}$ −24·75° in $CHCl_3$, and β-1 : 1-*diphenyl*-2 : 3 : 4 : 5-*di*iso*propylidenefructose* (III), b. p. 213·5°/0·3 mm., m. p. 194·5°, $[\alpha]_D^{18}$ −193·5° in $CHCl_3$, separable by fractional distillation; (III) is obtained almost exclusively when the Me ester of (I) is used. Hydrolysis of (II) with boiling PrOH–*N*-H_2SO_4 (1 : 1) affords 1-*phenyl*-d-*glucosone* (IV), m. p. 134·5°, $[\alpha]_D^{18}$ −17·72° in H_2O, −7·89° $\longrightarrow$ +7·18° in pyridine (*phenylhydrazone*, m. p. 154·5°; *tetra-acetate*, m. p. 128·5°, $[\alpha]_D^{18}$ +95·72° in $CHCl_3$, which could not be converted into a cryst. Br-derivative, and probably contains a free CO group), and a small amount of a *hydrocarbon*, $(C_{13}H_{10})_x$, m. p. 208·5°. (IV) reduces Fehling's solution and gives an intense reddish-violet coloration with hot conc. KOH (after 10 min. the reducing action disappears). (IV), $COMe_2$, and anhyd. $CuSO_4$ afford a 1-*phenyl*iso*propylideneglucosone*, m. p. 169°, $[\alpha]_D^{18}$ −93·35° in $CHCl_3$, which is also a reducing agent and does not give a coloration with KOH. Hydrolysis of (III) with PrOH–*N*-H_2SO_4 gives 1 : 1-*diphenyl*-2 : 3-iso*propylidene*-α-*fructofuranose*, m. p. 174°, $[\alpha]_D^{18}$ −99·3° in $COMe_2$ (unaffected by $COMe_2$ and anhyd. $CuSO_4$), and (mainly) 1 : 1-*diphenyl*-2 : 3-iso*propylidene*-d-*fructopyranose* (+0·25$CHCl_3$), m. p. 104°, $[\alpha]_D^{18}$ −149·6° in $COMe_2$ [reconverted by $COMe_2$ and $CuSO_4$ into (III)], both of which are non-reducing agents and are hydrolysed further to 1 : 1-*diphenyl*-d-*fructose* (+H_2O) (V), m. p. 81°, $[\alpha]_D^{18}$ +55·28° $\longrightarrow$ +42·28° in $COMe_2$ (*tetra-acetate*, m. p. 143°, $[\alpha]_D^{18}$ +3·18° in $COMe_2$). The first stage in the hydrolysis of (III) is fission of the oxide ring; the union of the 2 : 3-*iso*propylidene group is strengthened (by the electro-negative character of the Ph groups) at C_2, and formation of a 2 : 5-ring is possible. (V), $COMe_2$, and anhyd. $CuSO_4$ give 1 : 1-*diphenyl*-d-*fructose anhydride*, m. p. 149·5°, $[\alpha]_D^{18}$ +76·66° in $COMe_2$; the non-formation of an *iso*propylidene derivative demonstrates the furoid structure of (V).

(I) and $CH_2Ph{\cdot}MgCl$ give β-1 : 1-*dibenzyl*-2 : 3 : 4 : 5-*di*iso*propylidene*-d-*fructose* (VI), m. p. 121·5—122°, $[\alpha]_D^{18}$ −49·25° in $CHCl_3$, hydrolysed by PrOH–*N*-H_2SO_4 to 1 : 1-*dibenzyl*-2 : 3-iso*propylidene*-d-*fructopyranose*, m. p. 127—127·5°, $[\alpha]_D^{18}$ +32·95° in $CHCl_3$ [re-converted by $COMe_2$ and anhyd. $CuSO_4$ into (VI)], and 1 : 1-*dibenzyl*-α-*fructose* (VII), m. p. 149°, $[\alpha]_D^{18}$ +5·29° in $COMe_2$ (*tetra-acetate*, m. p. 94°, $[\alpha]_D^{18}$ +23·6° in $COMe_2$). (VII), $COMe_2$, and anhyd. $CuSO_4$ give 1 : 1-*dibenzyl*-4 : 5-iso*propylidene*-d-*fructopyranose*, m. p. 107°, $[\alpha]_D^{18}$ +7·29° in $COMe_2$, which is a reducing agent. H. BURTON.

Catalytic oxidation of *d*-glucose and related sugars by oxygen in presence of iron pyrophosphates. E. F. DEGERING and F. W. UPSON (J. Biol. Chem., 1931, **94**, 423—431).—The ease of oxidation (measured by the rate of formation of CO_2) of the following substances by O_2 in presence of a Fe pyrophosphate catalyst, prepared essentially by Spoehr's method (A., 1924, i, 836; 1926, 385), is in the order quoted: fructose, mannose, glucose, arabonic acid, arabinose, gluconic acid, α-methylmannoside, α-methylglucoside, mannitol, glycerol, glyceric acid, $OH{\cdot}CH_2{\cdot}CO_2H$, α-methylarabinoside, tetramethylglucose, tetraethyl-α-methylglucoside. CO_2 was not produced from the last two compounds under the experimental conditions, viz., first at 48° (16 days) and then at about 98° (7 days). The activity of the catalyst increases with rise in temp., and the rate of oxidation of the sugars is a function of the rate of enolisation. The probable intermediates in the oxidation processes are discussed. H. BURTON.

Non-fermenting constituents of the product obtained by the action of alkalis on hexoses (glutose). W. COLTOF (Biochem. Z., 1931, **243**, 191—224).—The syrups obtained by fermentation of molasses and by Lobry de Bruyn's method are both mixtures and are differently constituted. They give different mixtures of osazones and the reducing substances of the glucose fractions are not identical. Glutose is to be regarded as an unfermentable mixture containing hexose, biose, saccharic acids, protein, etc. P. W. CLUTTERBUCK.

Carbohydrates. XI. *al*-Glucose. P. BRIGL, H. MÜHLSCHLEGEL, and R. SCHINLE (Ber., 1931, **64**, [*B*], 2921—2934; cf. A., 1930, 1022; 1931, 71).—Treatment of *al*-glucose pentabenzoate with NH_3 in MeOH affords *glucosedibenzamide*, $OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_4{\cdot}CH(NHBz)_2$, m. p. 202° (decomp.), $[\alpha]_D^{21}$ +1·5° in pyridine. Since glucose does not condense with NH_2Bz in MeOH in presence of NH_3, the aldehydic form must be sufficiently stable to permit the separation of the Bz residues and the subsequent condensation. The prep. of less completely benzoylated *al*-glucose is difficult, since 1 mol. of BzCl and 1 mol. of glucose diethylmercaptal yield the Bz_4 derivative (cf. *loc. cit.*). Treatment of glucofuranose 3 : 5 : 6-tribenzoate with NH_3–MeOH affords NH_2Bz, glucose, and a small amount of glucosedibenzamide, indicating the probable presence of the aldehydic form in the initial material. Glucose Na H sulphite is immediately converted by Ac_2O into β-glucose penta-acetate and by MeOH containing NH_3 and NH_2Bz into glucose without a trace of the debenzamide compound. Mannose cyanohydrin is converted by ammoniacal $AgNO_3$ in presence of NH_2Bz solely into free mannose, whereas its Ac_6 derivative is transformed into *mannosediacetamide* (+H_2O), m. p. 219° (decomp.), and its *Bz_6* compound, m. p. 161—162°, $[\alpha]_D^{22}$ +30·3° in $CHCl_3$, into *mannose-dibenzamide*, m. p. 226° (decomp.), $[\alpha]_D^{24}$ +3·6° in pyridine, and *-monobenzamide*, m. p. (indef.) 254°. The presence of acidic groups therefore stabilises the aldehydic form. Measurements of the rate of addition of HCN to various sugars in H_2O in presence of a little NH_3 at 5·5—6·5° (as a possible means of determining the readiness of formation of the open from the cyclic form) show the following percentages of nitrile after 1·5 and 5 hr., respectively: glucose, 8·8 and 15·9; maltose, 6·6 and 11·9; lactose, 6·1 and 13·5; mannose, 35·9 and 75·4; galactose, 29·1 and 52·5; fructose, 25·6 and 40·5.

3 : 4 : 5 : 6-Tetrabenzoylglucose diethylmercaptal is transformed by $HgCl_2$ and $BaCO_3$ in boiling $COMe_2$ into al-*glucose* 3 : 4 : 5 : 6-*tetrabenzoate*, m. p. 220—222°, possibly a polymerised form. It behaves as a true aldehyde, being converted by MeOH–NH_3 into glucosedibenzamide, by NH_2Ph in EtOH into the *anilide*, $C_{40}H_{33}O_9N$, m. p. 118—120° after softening at 110°, by EtSH under certain conditions into the initial mercaptal, and by diazomethane into the *ketone*, $OBz{\cdot}CH_2{\cdot}[CH{\cdot}OBz]_3{\cdot}CH(OH){\cdot}COMe$, m. p. 194° (decomp.) after softening at 192°, $[\alpha]_D^{23}$ +48·9° in $CHCl_3$. *al*-Glucose tetrabenzoate and EtSH in absence of catalyst afford an impure *semimercaptal*; the *methylsemiacetal* has m. p. 215° (decomp.). EtSH in presence of $CHCl_3$ saturated with HCl converts *al*-glucose tetrabenzoate into 2-*ethylthiolglucose* 1 : 1-*diethylmercaptal* 3 : 4 : 5 : 6-*tetrabenzoate*, $OBz{\cdot}CH_2{\cdot}[CH{\cdot}OBz]_3{\cdot}CH(SEt){\cdot}CH(SEt)_2$, m. p. 84—85° after softening at 79°, $[\alpha]_D^{30}$ +57·6° in $COMe_2$, hydrolysed by NaOMe to 2-*ethylthiolglucose* 1 : 1-*diethylmercaptal*, m. p. 102° after softening at 101°, $[\alpha]_D^{25}$ +2·27° in $COMe_2$, and transformed by $HgCl_2$ and $BaCO_3$ in boiling $COMe_2$ into 2-*ethylthiol*-al-*glucose* 3 : 4 : 5 : 6-*tetrabenzoate*, m. p. 65—66°, $[\alpha]_D^{25}$ −42·7° in $COMe_2$. 2-*Ethylthiolmonobenzamide*, m. p. 186—190° (decomp.), is described. H. WREN.

Model experiments based on the theory of alcoholic fermentation. VI. Oxidation of mono- and di-*iso*propylideneglucose and of *iso*propylideneglucose 3-sulphuric acid. H. OHLE, G. COUTSICOS, and F. GARCIA Y GONZALEZ (Ber., 1931, **64**, [*B*], 2810—2813; cf. this vol., 144).—Oxidation of *iso*propylideneglucose at room temp. with $KMnO_4$ (=4·5O) affords K *iso*propylidenexyluronate, $[\alpha]_D^{20}$ −52·56° in H_2O, similarly obtained from di*iso*propylideneglucose; it evolves CO_2 when boiled with dil. mineral acids. *K di*iso*propylideneglucose* 3-*sulphate* (+2·5H_2O), $[\alpha]^{20}$ −13·17° in H_2O (also +0·5H_2O, decomp. 185—195°), is hydrolysed by *N*-H_2SO_4 at room temp. to *K* iso*propylideneglucose* 3-*sulphate*, $[\alpha]_D^{20}$ −14·56° in H_2O, oxidised by $KMnO_4$ to *K_2* iso*propylidenexyluronate*-3-*sulphate*, $[\alpha]_D^{20}$ −36·94°, obtained also from K *iso*propylidenexyluronate and pyridinium-*N*-sulphonic acid in pyridine. The course of the oxidation of di*iso*propylideneglucose 3-sulphuric acid resembles closely that of the parent compound. H. WREN.

Mechanism of carbohydrate oxidation. XIV. Alkaline degradation of cellobiose, lactose, melibiose, and gentiobiose by potassium hydroxide. W. L. EVANS and R. C. HOCKETT (J. Amer. Chem. Soc., 1931, 53, 4384—4400; cf. A., 1930, 1555).—The objectives in the work were: (1) to verify the prediction (based on maltose) that cellobiose and aq. solutions of KOH would give practically the same yields of lactic acid, AcOH, HCO_2H, and pyruvaldehydeosazone as maltose; (2) to verify the prediction that the glucosido-residues of cellobiose and gentiobiose and the galactosido-residues of lactose and melibiose would greatly influence the yields of lactic acid (yields relatively greater in the glucosidoglucoses); (3) to verify the prediction that owing to the hindering action of the hexosido-residue in the 4-hexosidoglucoses (cellobiose, lactose, and maltose, the yields of lactic acid would not be so great in these cases as from gentiobiose and melibiose (compounds in which the hexosido-attachment is on C_6). The reactions were found to be in harmony with these general points of view. Since pyruvaldehyde is regarded as the precursor of lactic acid, the same general relationships were also found in this case. The yields of AcOH from the 6-hexosidoglucoses were greater than those obtained from the 4-hexosidoglucoses, whilst those of HCO_2H show the opposite tendency. The disaccharides show a max. yield of AcOH quite similar to that of the hexoses. A mechanism for the formation of AcOH and HCO_2H from the disaccharides is given. On the enediol theory of action in the dissacharides, the probable oxidation products of gentiobiose and melibiose are given. The interpretation of the max. point in the curve of lactic acid production from gentiobiose and melibiose is based on the assumption that a 6-hexosidoglucose-4 : 5-enediol must have formed in each case in the regions of higher alkalinity. A mechanism is given to explain the decreasing yield of this acid after the point of max. production has been passed. The results are given in a series of curves. C. J. WEST (*b*).

Novel modification of lactose. R. C. HOCKETT and C. S. HUDSON (J. Amer. Chem. Soc., 1931, **53**, 4455—4456).—Finely-powdered α-lactose monohydrate, shaken at room temp. with 10 times its wt. of MeOH containing 1—5% of HCl, changes to a needle type of crystal, considered to be a mol. compound, *α-lactose–β-lactose* (5 : 3), $[\alpha]_D^{20}$ +67·9° (initial)⟶ +55·2° (anhyd. lactose) in H_2O. A mixture of the α- and β-forms of lactose in the ratio of 5 : 3 would have initial $[\alpha]_D$ +67·5°. The new compound is anhyd., whereas α-lactose has never been obtained anhyd. by crystallisation. C. J. WEST (*b*).

***l*-Glucoside of *Asphodeles*.** H. COLIN and C. NEYRON (Bull. Soc. chim., 1931, [iv], **49**, 1542—1547).—Fresh *Asphodeles* tubercles contain about 8% of lævulosan, 1% of sucrose, and 0·5% of reducing sugar. The glucoside obtained by aq. extraction, $[\alpha]_D^{15}$ −18·6°, darkens at 170° and decomposes at about 210° and is hydrolysed at p_H about 4 in 0·25 hr., yielding mainly fructose together with some glucose. When this mixture is treated with CaO, a sugar, $[\alpha]_D^{25}$ −86°, is regenerated from the Ca complex, the sugar obtained from the mother-liquors having $[\alpha]_D^{25}$ −41°, indicating the presence of a second glucoside constituent. The latter is slowly oxidised by Br and

I in weak alkaline media, the reducing power of the asphodeloside decreasing about 16% in presence of Br and about 40% in abs. EtOH with the less sol. fractions, indicating the presence of about 1 mol. of glucose to 5—6 mols. of fructose. The glucoside is rapidly hydrolysed by mycelian powder or by *Aspergillus niger*, but is only slowly and partly attacked by yeast-invertase. Living yeast readily ferments both *Asphodeles* sap and the purified glucoside. The latter is probably a glucofructosan or an intimate mixture of fructosan and glucosan.

R. Brightman.

[Highly-polymerised compounds. LVI.] K. H. Meyer and H. Mark (Ber., 1931, 64, [*B*], 2913).—A reply to Staudinger (this vol., 46). H. Wren.

Polymorphism of substances of high mol. wt. II. Amorphous and crystalline inulin. J. R. Katz and A. Weidinger (Rec. trav. chim., 1931, **50**, 1133—1137).—*X*-Ray examination of ordinary inulin and of Berner's form readily sol. in cold H_2O (A., 1931, 716) shows the latter to be a genuine amorphous form slightly contaminated with a cryst. modification. The amorphous form, although stable when dry, rapidly reverts to the ordinary form in moist air. Schlubach and Elsner's β-inulin (A., 1930, 1415) appears to be the same as Berner's prep.

C. W. Davies.

Oxidation of cellulose. T. Nakashima (J. Soc. Chem. Ind. Japan, 1931, **34**, 414—418B).—On continued oxidation of "biosan acetate" by O_2 in the presence of NaOH, the I val. decreases, whilst the acid val. increases, showing that the CHO groups are oxidised to CO_2H. Determination of residual cellulose by $K_2Cr_2O_7$ shows that the amount of cellulose decomposed increases with increasing time of oxidation. It is suggested that the reaction proceeds chiefly by oxidation of CHO to CO_2H groups and by decomp. of the terminal glucose residues containing CO_2H to acids of lower mol. wt. When the end glucose residue is decomposed a new CHO group is liberated which is oxidised to CO_2H, and so on. Shortening of the micellar chains must proceed gradually because oxidation takes place mainly at the ends. This is supported by the fact that the viscosity of the material decreases only slowly during the reaction. In the similar oxidation of glucose, the I val. decreases, and the acid val. increases, rapidly. B. P. Ridge.

***X*-Ray examination of cellulose derivatives. XI. Additive compounds of cellulose with hydrazine, ethylenediamine, and tetramethylenediamine.** C. Trogus and K. Hess (Z. physikal. Chem., 1931, **B, 14**, 387—395; cf. A., 1931, 1219).—The existence of additive compounds of cellulose with the above bases has been demonstrated by *X*-ray examination. The base is directed across the fibre axis of the cellulose crystallite. These compounds are decomposed on treatment with H_2O.

R. Cuthill.

Least equivalent of β-cellulose, tunicin, and cotton cellulose. E. Schmidt, W. Simson, and R. Schnegg (Naturwiss., 1931, **19**, 1006—1007).—The least equiv. of β-cellulose, tunicin, and cotton (Indian and American) cellulose is 96 $C_6H_{10}O_5$, the same as for cellulose derived from deciduous and coniferous trees (A., 1931, 827). W. R. Angus.

Decomposition of quaternary ammonium hydroxides. VI. J. von Braun and E. Anton (Ber., 1931, **64**, [*B*], 2865—2869).—Methylation of primary, sec., and tert. bases with Me_2SO_4 affords quaternary salts with the group $\cdot O\cdot SO_2\cdot OMe$ which can be salted out with conc. alkali and purified by dissolution in $CHCl_3$ and pptn. with Et_2O. With boiling aq. $Ba(OH)_2$, they gradually yield $BaSO_4$ and the hydroxide, but hydrolysis is preferably effected with boiling H_2SO_4. Addition of $Ba(OH)_2$ to the resulting solution ppts. $BaSO_4$ in a readily filtered form; the filtrate is conc., any $BaCO_3$ is removed, and after addition of KOH the residual solution is distilled. Thus *n*-hexylamine is converted through the *quaternary methosulphate*, m. p. 90°, into Δ^{β}-hexene (yield 60%) and dimethyl-*n*-hexylamine, b. p. 146° (yield about 20%); piperidine affords "dimethylpiperidine," b. p. 117—118°, and NEt_3 yields $NMeEt_2$, b. p. 65° (yield 50%). αμ-Diaminododecane, b. p. 187°/16 mm., m. p. 66—67°, is transformed through the quaternary *salt*, m. p. 186°, into $\Delta^{\alpha\lambda}$-*dodecadiene*, b. p. 207° (yield 65%), and *dimethyl*-Δ^{λ}-*dodecenylamine*, $CH_2{:}CH\cdot[CH_2]_{10}\cdot NMe_2$, b. p. 132—135°/16 mm. (yield 25%) [*picrate*, m. p. 127°]. The oily naphthenic acid, $C_{18}H_{34}O_2$, from Galician petroleum (A., 1931, 1396), is converted into the *naphthenamine*, $C_{17}H_{33}\cdot NH_2$, b. p. 175—195°/16 mm., which yields a *hydrocarbon*, $C_{17}H_{32}$, b. p. 155—175°/16 mm. (yield 63%), and a basic fraction, $C_{17}H_{33}NMe_2$, b. p. 175—195°/16 mm. (yield 31%). H. Wren.

Existence of molecular compounds between amino-acids in solution and in the solid state. M. Frankel (Biochem. Z., 1931, **242**, 67—87).—Examination of mixed solutions of the following pairs of substances: *d*-arginine and *l*-aspartic acid; *d*-arginine and *d*-glutamic acid; *d*-arginine and *l*-proline; *d*-arginine and *l*-oxyproline; *l*-histidine and *l*-aspartic acid; *l*-histidine and *d*-glutamic acid; *l*-histidine and *l*-proline; *l*-histidine and *l*-oxyproline, by the cryoscopic and refractometric methods shows that double compounds are present in each case. The isolation of mol. compounds from *d*-arginine with *l*-aspartic acid and *d*-arginine with *d*-glutamic acid is described. P. W. Clutterbuck.

Elimination of halogen by dilute alkali from stereoisomeric halogenoacylamino-acids. Configuration of optically active α-halogeno-fatty acids. V. E. Abderhalden and F. Schweitzer (Fermentforsch., 1931, **13**, 115—125; cf. A., 1931, 1150).—Fractional crystallisation of dl-α-*bromo*iso*valeryl*-dl-*leucine*, m. p. 105—126°, gave the racemic compounds *A*, m. p. 164°, and *B*, m. p. 118—119°. The four optically active forms of α-bromo*iso*valeryl-leucine were obtained: *l*-*l*- (I), m. p. 142—143°, $[\alpha]^{23}_{D}$ −50·0°; *l*-*d*- (II), m. p. 141—142°, $[\alpha]^{23}_{D}$ +5·0°; *d*-*d*- (III), m. p. 145°, $[\alpha]^{23}_{D}$ +52·0°; *d*-*l*- (IV), m. p. 143—144°, $[\alpha]^{23}_{D}$ −5·0°. (I) and (III) gave compound *A*, (II) and (IV), *B*. The four active forms of α-*bromo*-iso*valeryl*nor*leucine* were prepared: *l*-*d*- (V), m. p. 113°, $[\alpha]^{23}_{D}$ −11·3°; *l*-*l*- (VI), m. p. 111°, $[\alpha]^{22}_{D}$ −38·3°; *d*-*l*- (VII), m. p. 104—108°, $[\alpha]^{22}_{D}$ +12·7°; *d*-*d*- (VIII), m. p. 111—112°, $[\alpha]^{22}_{D}$ +36·0° (all rotations in 99%

EtOH). The racemate *A*, but not *B*, was hydrolysed by trypsin-kinase, *B* was hydrolysed more rapidly than *A* by 0·5*N*-NaOH. Of compounds (I) to (VIII) only (I) and (VI) were hydrolysed by trypsin-kinase.
J. H. Birkinshaw.

Neutral salt additive compounds of β-alanine. H. King and G. V. Rutterford (J.C.S., 1931, 3131—3134).—The following additive *compounds* are prepared from β-aminopropionic acid (=A) and the appropriate salt in conc. aq. solution: A,LiCl,1·5H_2O; A,LiBr,1·5H_2O; A,LiI,1·5H_2O; A_2,LiI,1·5H_2O; A,NaI; A_2,$CaCl_4$,2H_2O; A,$CaBr_2$,4H_2O; A_2,$CaBr_2$,3H_2O; A,CaI_2,4H_2O; A,$SrCl_2$,4H_2O; A,$SrBr_2$,4H_2O; A,SrI_2,4H_2O; A,$BaBr_2$,2H_2O. Compounds could not be obtained from NaCl, NaBr, KCl, KBr, KI, and $BaCl_2$.
H. Burton.

Preparation of crystalline ornithine. Picrates and monosulphates of ornithine. H. B. Vickery and C. A. Cook (J. Biol. Chem., 1931, 94, 393—399).—Addition of MeCHO-free EtOH and Et_2O to a conc. aq. solution of *d*-ornithine [mono- and di-picrates, both decomp. 208° after darkening at about 200°; *monosulphate*, decomp. 234° (darkens about 225°)] gives a partly cryst. product, m. p. 140° (softens at 120°), $[\alpha]_D^{25}$ +11·5° in H_2O, which is not completely stable even in the dark. *dl*-Ornithine monosulphate has m. p. 234° (decomp.) (darkens slightly from 225°) (lit. 213°).
H. Burton.

Synthesis of glutamic acid. M. S. Dunn, B. W. Smart, C. E. Redemann, and K. E. Brown (J. Biol. Chem., 1931, 94, 599—609).—Et oximinomalonate is reduced by Al–Hg (method of prep. given) using Cerchez's procedure (A., 1931, 205) to Et aminomalonate (I). *Et benzamidomalonate*, m. p. 62—63°, Et β-bromopropionate, and EtOH–NaOEt give *Et α-benzamidopropane-ααγ-tricarboxylate*, decomp. on attempted distillation under 4 mm. pressure, hydrolysed by conc. HCl to *dl*-glutamic acid (II) in 52% yield. (I), Et β-chloropropionate, and EtOH–NaOEt afford Et α-aminopropane-ααγ-tricarboxylate [probably contaminated with some of the *N*-β-carbethoxyethyl derivative of (I)], also hydrolysed to (II) in 36% yield. Photomicrographs of *d*-glutamic acid and (II) are given.
H. Burton.

Alkaline deamination of derivatives of cysteine. H. T. Clarke and J. M. Inouye (J. Biol. Chem., 1931, 94, 541—550).—*S*-Ethylcysteine (I) is obtained in 75% yield when cystine is reduced with Sn and 10% HCl, the mixture basified with aq. EtOH–NaOH, and then treated with Et_2SO_4. *S*-Benzylcysteine (II) is similarly prepared in 62% yield using CH_2PhCl in place of Et_2SO_4, whilst *S*-phenylcysteine (III) is formed in 30% yield when cysteine is treated with diazotised NH_2Ph in neutral solution. The reactivity of these compounds towards alkaline deaminating agents is (I)<(II)<(III). Cystine, which is more reactive than cysteine (A., 1931, 76), occupies a position intermediate between (II) and (III). The stability of these compounds towards alkalis is influenced by the degree of unsaturation of the group attached to the S atom. Cysteic acid is deaminated at a much slower rate than cysteine and its derivatives. The deaminating agents used were those previously employed (*loc. cit.*).
H. Burton.

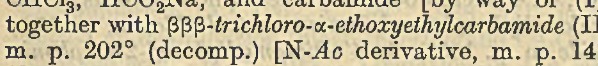
Alkyl- and dialkyl-ammonium dithiocarbamates and trithiocarbonates and dialkylideneammonium alkylidenedithiocarbamates. T. G. Levi (Gazzetta, 1931, 61, 803—814).—*Benzyl-* [m. p. 90—93° (decomp.)], *camphyl-* [m. p. 100—104° (decomp.)], *diethyl-* [m. p. 98—105° (decomp.)], *dipropyl-* [m. p. 80—90° (decomp.)], *diisobutyl-* [m. p. 83—93° (decomp.)], *piperidyl-* [m. p. 80—90° (decomp.)], *dibenzyl-* [m. p. 145—155° (decomp.)], and *phenylmethyl-* (partly melts below 100°) *-ammonium dithiocarbamates* are obtained from NH_4 dithiocarbamate and the hydrochloride of the corresponding amine. *Dimethylammonium pentamethylenedithiocarbamate*, m. p. 84—86°, *diisobutylammonium dimethyldithiocarbamate*, m. p. 84—86°, and *dithiocarbamates* of *s*- [m. p. 98—100° (decomp.)] and *as*-diphenylguanidine, *s*-ditolylguanidine [m. p. 130—132° (decomp.)], *s*- (m. p. 88—90°), and *as*- (m. p. 103—106°) -triphenylguanidine, quinine (m. p. 107—109°), quinidine (m. p. 202—205°), cinchonine (m. p. 208—209°), strychnine (m. p. above 250°), and brucine (m. p. about 140°), *dimethyldithiocarbamates* of quinine and strychnine, *strychnine pentamethylenedithiocarbamate*, and *benzyl-* and *dipropyl-ammonium trithiocarbonates* are similarly obtained. *Diethyl-* (m. p. 82—83°), *dipropyl-* (m. p. 81—82°), and *diisobutyl-* (m. p. 101°) *-ethylideneammonium ethylidenedithiocarbamates* are obtained from dialkylammonium dithiocarbamates and MeCHO. With CH_2O there is no reaction. *Benzylammonium dithiocarbamate* reacts with CH_2O giving a *compound*, $C_{10}H_{12}N_2S_2$, m. p. 130°, and with MeCHO giving a *compound*, $C_{12}H_{16}N_2S_2$, m. p. 98°. Dimethylammonium propyldithiocarbamate with CH_2O gives a *compound*, $C_7H_{15}N_2S_2$, m. p. 52°.
E. E. J. Marler.

Purification and some physical properties of formamide. G. F. Smith (J.C.S., 1931, 3257—3263).—Data are recorded for *d*, η, and γ for $HCONH_2$, which, when purified by freezing in absence of atm. H_2O, has m. p. 2·55°. The parachor is 2% and 0·7% low at 18° and 50°, respectively, possibly owing to association at low temp.
R. S. Cahn.

Constitution of synthetic resins. II. Theoretical basis and quantitative study of carbamide-formaldehyde condensation. G. Walter and M. Gewing (Kolloid-Beih., 1931, 34, 163—217; cf. A., 1931, 1398).—A quant. study of the resinification of di(hydroxymethyl)carbamide (I) on fusion and subsequent heating in presence of condensing agents, and also of the condensation of (I) or of equiv. amounts of CH_2O and $CO(NH_2)_2$ in aq. solution, and of fusion of (mono)hydroxymethylcarbamide. The course of resinification is followed by determination of the H_2O and CO_2 evolved and analysis of the final resin, which indicates that the composition of the glass-clear resin is approx. the mean of those of (I) and hydroxymethylmethylenecarbamide (II), whilst those of the turbid resins approach that of (II). Fusion of (I) to a clear liquid can only be carried out either in small quantities by extremely rapid heating or in presence of basic substances, *e.g.*, NaOAc; slow heating, or heating in contact with traces of acid, leads to evolution of CH_2O and formation of an amorphous mass of (II). If a small quantity of acid be added and heating continued to 150° further condensation occurs with elimination of CH_2O and H_2O and a transparent resin is produced. An optimum p_H exists for this stage, and in aq. solution is approx. 3·0—5·0; within these limits, and close to p_H 5·0, a narrower range exists within which gelatinisation can be controlled. Further condensation of this type does not occur in presence of basic catalysts which cannot bring about elimination of CH_2O.

It is considered that the final resins contain the $>N\cdot CH_2\cdot N<$ and $\cdot CH_2\cdot OH$ groups, although the former cannot be detected by a Herzig–Meyer determination. Methylene-carbamide, -thiocarbamide, and -bisacetamide, and hexamethylenetetramine also give low results by this method. The structure of the carbamide–CH_2O resins is discussed, and units of a chain structure, probably linked by covalencies into a three-dimensional network, are considered most probable. The peptisation of (II) by aq. CH_2O, and formation of a transparent resin from the product in the usual manner, is regarded as evidence that in this case at least the resin is a solution of $\cdot CH_2\cdot OH$-free substances in $\cdot CH_2\cdot OH$ derivatives, an explanation which is also in agreement with the properties of the initial solution. H. A. Piggott.

Condensation of chloral with carbamide and phenylcarbamide. F. D. Chattaway and E. J. F. James (Proc. Roy. Soc., 1931, **A, 134**, 372—384).—α-Hydroxy-βββ-trichloroethylcarbamide (I) (modified prep.), m. p. 150° (decomp.), is hydrolysed by hot aq. EtOH or by keeping in aq. NaOH to $CHCl_3$, HCO_2H, and carbamide, but is pptd. unchanged on immediate acidification of its solution in aq. NaOH. (I), Ac_2O, and a drop of H_2SO_4 give N-(βββ-*trichloro-α-acetoxyethyl*)-N′-*acetylcarbamide*, m. p. 160° (decomp.), but (I), Ac_2O, and cold *N*-NaOH give *di*-(*α-carbamido*-βββ-*trichloroethyl*) *ether*, $[NH_2\cdot CO\cdot NH\cdot CH(CCl_3)]_2O$, m. p. 222° (decomp.) [(α-N′-*Ac*)$_2$ derivative, m. p. 241° (decomp.); (α-NN′-*Cl*$_2$)$_2$ derivative (prepared by Cl_2 in AcOH), m. p. 131° (decomp.)], which with Na in EtOH yields $CHCl_3$, HCO_2Na, and carbamide [by way of (I)], together with βββ-*trichloro-α-ethoxyethylcarbamide* (II), m. p. 202° (decomp.) [N-*Ac* derivative, m. p. 142° (decomp.)]. The following substances were similarly prepared, the group named being the α-substituent: *MeO*-, m. p. 205° (decomp.) [N-*Ac* derivative, m. p. 154° (decomp.)]; $Pr^{\alpha}O$-, m. p. 177° (decomp.); $Pr^{\beta}O$-, m. p. 180° (decomp.); $Bu^{\alpha}O$-, m. p. 165° (decomp.).

Di-(α-hydroxy-βββ-trichloroethyl)carbamide (modified prep.), m. p. 194° (decomp.), is hydrolysed by keeping in aq. NaOH; with Ac_2O and a drop of H_2SO_4 it forms s-*di*-(βββ-*trichloro-α-acetoxyethyl*)*carbamide*, m. p. 189° (decomp.), but with Ac_2O and *N*-NaOH gives *anhydrodichloralcarbamide*, probably  $O<\begin{matrix}CH(CCl_3)\cdot NH\cdot CO\cdot NH\cdot CH(CCl_3)\\ CH(CCl_3)\cdot NH\cdot CO\cdot NH\cdot CH(CCl_3)\end{matrix}>O$ (III), m. p. 137°, which with Na in EtOH forms $CHCl_3$, HCO_2Na, carbamide, and s-*di*-(βββ-*trichloro-α-ethoxyethyl*)*carbamide* (IV), m. p. 241° (decomp.); the corresponding α-*MeO*- and α-$Pr^{\alpha}O$-compounds, m. p. 234° (decomp.) and 224° (decomp.), respectively, were similarly prepared. (II) and chloral at 100° form N-(βββ-*trichloro-α-ethoxyethyl*)-N′-(βββ-*trichloro-α-hydroxyethyl*)*carbamide* (V), m. p. 147° (decomp.) [N′-α-*AcO*-derivative, m. p. 187° (decomp.)]; the corresponding N-α-*MeO*-compound, m. p. 159° (decomp.) [N′-α-*AcO*-derivative, m. p. 189° (decomp.)], was similarly prepared. (V) with Ac_2O and *N*-NaOH gives *bis*-[α-(N′-βββ-*trichloro-α-ethoxyethylcarbamido*)-βββ-*trichloroethyl*] *ether*, $[CCl_3\cdot CH(OEt)\cdot NH\cdot CO\cdot NH\cdot CH(CCl_3)]_2O$; this, when kept with Na in EtOH, affords (IV), and with Na in MeOH or PrOH affords N-(βββ-*trichloro-α-ethoxyethyl*)-N′-(βββ-*trichloro-α-methoxyethyl*)*carbamide* and the corresponding N′-(α-$Pr^{\alpha}O$)-compound, m. p. 212° (decomp.) and 228° (decomp.), respectively. Phenylcarbamide, chloral hydrate (2·5 mols.), and HCl, when kept, deposit N-*phenyl*-N′-(βββ-*trichloro-α-hydroxyethyl*)*carbamide*, m. p. 142° (decomp.) (decomposes when kept or warmed in aq. NaOH) [*Ac*$_2$ derivative, m. p. 104° (decomp.)], which with Ac_2O and *N*-NaOH gives *di*-α-(βββ-*trichloro*-N′-*phenylcarbamidoethyl*) *ether*, $[NHPh\cdot CO\cdot NH\cdot CH(CCl_3)]_2O$, m. p. 236° (decomp.) after decomp. from 195° [N′-*Ac*$_2$ derivative, m. p. 153° (decomp.)]; this with Na in EtOH affords N-*phenyl*-N′-βββ-*trichloro-α-ethoxyethylcarbamide*, m. p. 153° (decomp.) [N-*Ac* derivative, m. p. 88° (decomp.)]; the corresponding α-*MeO*-compound, m. p. 189° (decomp.) [N-*Ac* derivative, m. p. 102° (decomp.)], was similarly obtained. R. S. Cahn.

Supposed optical activity of ethyl diazosuccinate. A. Weissberger and R. Haase (Ber., 1931, 64, [*B*], 2896—2905).—The action of $NaNO_2$ and HCl on Et_2 aspartate leads in all cases to dextrorotatory products. Decomp. of the products with dil. acids causes evolution of less than the calc. amount of N_2 and does not affect the sp. rotation. Since the optical activity is unaffected by catalytic hydrogenation of the product in presence of colloidal Pd, it cannot be due to Et diazosuccinate, but is attributed to an impurity. The product contains Cl, but activity cannot be ascribed to Et_2 chlorosuccinate, since diazotisation in presence of H_2SO_4 affords an optically active material. The possible presence of Et_2 *d*-malate harmonises approx. with the deficit of N_2 and the optical activity of the product and, if this is accepted, the production of *d*-bromosuccinic acid by treatment of the diazo-ester with HBr in Et_2O loses validity as evidence of the existence of optically active diazo-ester (cf. Levene and Mikeska, A., 1923, i, 25, 663). Since, however, *l*-aspartic acid is converted by HNO_2 into *l*-malic acid, the exact nature of the impurity is uncertain. The data with regard to optically active diazosuccinic (and other aliphatic diazo-) esters should be deleted from the literature. H. Wren.

Action of arsenic chloride on ethyl sodiomalonate. II. Reply to Guglialmelli and Ruíz. E. V. Zappi (Anal. Asoc. Quim. Argentina, 1931, 19, 80—81; cf. A., 1930, 899; 1931, 832).—Polemical. R. K. Callow.

Action of fluorine on aromatic compounds and a theory of ring substitution. S. F. Whearty, jun. (J. Physical Chem., 1931, 35, 3121—3147).—Very small quantities of impure $C_6Cl_4F_2$, b. p. 230—240°, and of $C_6Cl_3F_3$ have been obtained from F and C_6Cl_6. From *s*-$C_6H_3Cl_3$ some $C_6HF_3Cl_2$, b. p. 75°/25 mm., was formed. Interaction of F with other C_6H_6 derivatives gave explosions or negative results. The interpretation of the interaction of a halogen with a C_6H_6 compound is discussed at length.

A. L. Henne (*b*).

Thermal vapour-phase chlorination of toluene and benzene. J. Mason, C. A. Smale, R. N. Thompson, and T. S. Wheeler (J.C.S., 1931, 3150—3157).—Cl_2 reacts rapidly (cf. A., 1931, 1267) with PhMe above 250° to give CH_2PhCl and $CHPhCl_2$; in presence of carriers nuclear substitution also occurs. With C_6H_6 above 400° PhCl and $C_6H_4Cl_2$ are formed. The proportions of first- and second-stage products agree well with theory.

C. W. Davies.

Compound of nitrobenzene and sulphuric acid. I. Masson (J.C.S., 1931, 3200—3206).—$PhNO_2$ and H_2SO_4, m. p. 10·35°, form the compound $PhNO_2,H_2SO_4$, m. p. 11·6°, which is probably $[PhNO_2\cdot H]^+[HSO_4]^-$, since it increases the conductance of H_2SO_4. This compound is unimol. in H_2SO_4, but bimol. in C_6H_6. Its influence in substitution reactions is discussed. Pure C_6H_6 and $PhNO_2$ have m. p. 5·58° and 5·84°, respectively. R. S. Cahn.

Action of sodamide on some bromohydrocarbons. (Mlle.) P. Amagat (Bull. Soc. chim., 1931, [iv], 49, 1410—1417; cf. A., 1930, 759).—β-Phenylpropyl bromide, β-phenylbutyl bromide, and β-phenyl*iso*amyl bromide are stable towards H_2O and 0·1*N*-$AgNO_3$ and are not isomerised in ultra-violet light (cf. A., 1928, 255). γ-Phenylpropyl bromide, b. p. 120—122°/16 mm., is obtained in 85% yield from PBr_3 and γ-phenylpropyl alcohol, but under the same conditions β-phenyl-β-ethylbutyl alcohol is dehydrated, giving a hydrocarbon, b. p. 110—115°/12 mm. β-Phenyl-β-benzylbutyl alcohol similarly yields an olefine, b. p. 180°/15 mm. 48% HBr and β-phenyl-β-ethylbutyl alcohol afford only 20% of the bromide, the alcohol being mainly dehydrated to *α-phenyl-β-ethyl-Δ^{α}-butene*, b. p. 114—118°/12 mm. In xylene γ-phenylpropyl bromide is unattacked by $NaNH_2$, but in CH_2Ph_2 a mixture of sec. and tert. amines is obtained. R. Brightman.

Diphenyl and its derivatives. VIII. 2 : 2′-Disubstituted derivatives of diphenyl. L. Mascarelli and D. Gatti [with M. Pirona] (Gazzetta, 1931, 61, 782—797).—2-*Chloro*-, m. p. 71°, 2-*bromo*-, m. p. 66—67°, 2-*iodo*-, m. p. 81—82°, and 2-*acetoxy*-, m. p. 102°, -2′-*nitrodiphenyl* are obtained from 2′-nitro-2-aminodiphenyl. The Sandmeyer reaction with 2′-nitro-2-aminodiphenyl gives mainly products containing a heterocyclic nucleus, *e.g.*, carbazole; diazotisation in presence of Cu˙ halide in a current of CO gives better results. 2-*Chloro*-, m. p. 56—57° (hydrochloride, m. p. 176—177°), 2-*bromo*-, m. p. about 46—50°, b. p. 196—197°/27 mm., and the *Ac* derivative of 2-*iodo*-2′-*aminodiphenyl* are obtained by reduction of the corresponding halogeno-nitro-compounds. 2-*Chloro*-2′-*bromo*-, m. p. 58°, and 2-*chloro*-2′-*iodo-diphenyl*, m. p. 63—64°, are obtained from 2-chloro-2′-aminodiphenyl, and 2′-*bromo*-2-*iododiphenyl*, m. p. 90°, from 2-bromo-2′-aminodiphenyl. The yields in all cases are small in comparison with the 3 : 3′ and 4 : 4′ series. 2-*Chloro*- and 2-*bromo*-2′-*nitrodiphenyl* are also obtained by the action of Cu on a mixture of *o*-iodonitro- and *o*-chloro- (or bromo-)iodobenzene. E. E. J. Marler.

Iodo-derivatives of diphenyl obtained by direct action of iodine in presence of nitric acid. I. 4-Iodo-4′-nitrodiphenyl. L. Guglialmelli and M. R. Franco (Anal. Asoc. Quím. Argentina, 1931, 19, 5—33).—The following conditions are optimal for the preparation of 4-*iodo*-4′-*nitrodiphenyl*, m. p. 202—206° (*dichloride*, m. p. 190°): HNO_3 (*d* 1·40) (12—24 c.c.) is added dropwise during 30 min. to a mixture of Ph_2 (10 g.) and I (5 g.) at 100°. The product, washed free from acid, is then freed from (?) 2 : 4′- and 4 : 2′-compounds by extraction with EtOH. Iodination probably precedes nitration. The substance is identical with the product obtained from 4-nitro-4′-aminodiphenyl by the diazo-reaction, and reduction yields 4-iodo-4′-aminodiphenyl, m. p. 159°, identical with the substance prepared from benzidine and yielding identical derivatives (*benzylidene*, m. p. 208·5—209·5°; p-*dimethylaminobenzylidene*, m. p. 204°, and *piperonylidene*, m. p. 150—151°).

R. K. Callow.

Ditolyls. III. Derivatives of 2′-nitro-*dl*-2-amino-6 : 6′-ditolyl. A. Angeletti (Gazzetta, 1931, 61, 832—838).—2-*Iodo*- (m. p. 129—130°), 2-*bromo*- (m. p. 122—123°), and 2-*chloro*- (m. p. 99—100°) -2′-*nitro*-6 : 6′-*dimethyldiphenyls* are obtained from 2′-nitro-2-amino-6 : 6′-dimethyldiphenyl by the Sandmeyer reaction. 2′-*Nitro*-2-*hydroxy*-6 : 6′-*dimethyldiphenyl* (*Ac* derivative, m. p. 86—87°) could not be isolated in a pure state. E. E. J. Marler.

Conversion of halogenodiphenylenesulphones into halogenodiphenyl-2-sulphonic acids. C. Courtot and R. Evain (Bull. Soc. chim., 1931, [iv], 49, 1555—1562; cf. A., 1931, 1281, 1406).—Benzidinesulphone is converted by diazotisation and decomp. with EtOH into diphenylenesulphone (yield 78%), m. p. 232°. 4 : 4′-Dichloro-, m. p. 295—296°, and 4 : 4′-dibromo-diphenylenesulphone, m. p. 313°, are obtained in 85% yield. On alkaline fusion at 190—200°, 4 : 4′-dichlorodiphenylenesulphone affords 4 : 4′-*dichlorodiphenyl-2-sulphonic acid* (*chloride*, m. p. 75°; *amide*, m. p. 155°). 4 : 4′-*Dibromodiphenyl-2-sulphonic acid* (*chloride*, m. p. 123°; *amide*, m. p. 188°) is similarly obtained at 200—210°. R. Brightman.

Action of scission catalysts in hydrogenative cracking of polynuclear hydrocarbons. A. Kling and D. Florentin (Compt. rend., 1931, 193, 1198—1199).—The decomp. of $C_{10}H_8$ and anthracene in H_2 at 475—492° and 225—290 kg. per sq. cm. in presence of hydrogenating catalysts, *e.g.*, NiO, MoS_2, and Mo oxides, gives small amounts of benzenoid hydrocarbons, the yields of which are improved by addition of S or H_2SeO_3. Much better results are obtained with $AlCl_3$ in absence of H_2O. H. A. Piggott.

Nitro-derivatives of naphthalene, tetrahydronaphthalene, and dinaphthyl. W. M. Cumming and G. Howie (J.C.S., 1931, 3176—3181).—4-*Iodo*-2-*nitro*- (I), m. p. 192—193°, and 2-*iodo*-4-*nitro*- (II), m. p. 234°, -α-*naphthylamine* are prepared by iodinating 2- and 4-nitro-α-naphthylamine, respectively, with ICl in AcOH. 1-*Iodo*-3-*nitro*-, m. p. 118—118·5°, 2-*iodo*-1-*nitro*-, m. p. 84°, 2-*iodo*-3-*nitro*- (III),

m. p. 76—76·5°, and 3-*iodo*-1-*nitro*- (IV), m. p. 64—65°, -ar-*tetrahydronaphthalene* are prepared by the usual method from the appropriate nitrotetrahydronaphthylamines. Oxidation of (III) and (IV) with Br gives 2-*iodo*-3-*nitro*-, m. p. 89—89·5°, and 3-*iodo*-1-*nitro*-, m. p. 108°, -*naphthalene*, respectively; the last-named is also prepared by elimination of NH_2 from (II). Deamination of (I) affords 1-iodo-3-nitronaphthalene, m. p. 147° (lit. 142—143°). Ullmann's generalisations (A., 1901, i, 586; 1904, i, 725) for the prep. of *s*-diphenyls hold also in the $C_{10}H_8$ and tetrahydronaphthalene series. Condensation of halogenonitronaphthalenes could not be effected by Na. The following are prepared by Ullmann's method: 1 : 1′-, m. p. 187—188°, and 3 : 3′- (V), m. p. 201°, -*dinitro*-2 : 2′-*ditetrahydrodinaphthyls*; 2 : 2′-, m. p. 187° (lit. 179—180°) [Chudožilov's method (A., 1925, i, 903) (modification described) does not give trustworthy results], and 3 : 3′-, m. p. 281° (lit. 262—264°), -dinitro-1 : 1′-dinaphthyls; 1 : 1′-dinitro-2 : 2′-dinaphthyl, m. p. 284° (decomp.) (lit. 264—265° and 276°). 3 : 3′-*Dinitro*-2 : 2′-*dinaphthyl*, m. p. 257—258°, is prepared by oxidation of (V) with Br. 4 : 4′-Dinitro-1 : 1′-dinaphthyl, m. p. 246°, obtained by Schoepfle's method (A., 1923, i, 776), could not be prepared from 4-nitronaphthalene-1-diazonium sulphate and Cu. 2 : 2′-Dinaphthyl and HNO_3 (*d* 1·42) in AcOH give 1-*nitro*-2 : 2′-*dinaphthyl*, m. p. 179°, nitrated further to a mixture, m. p. 198—208°, of dinitro-isomerides containing the 1 : 1′-derivative, since reduction with Zn dust and conc. HCl in AcOH affords 1 : 1′-imino-2 : 2′-dinaphthyl. The mixture of 1- and 2-nitrotetrahydronaphthalenes obtained from tetrahydronaphthalene, b. p. 95—97°/16 mm. (lit. above 175°/13 mm.), by a modification of Schroeter's method (A., 1922, i, 123), is reduced by Veselý and Chudožilov's method (A., 1925, i, 654); a simple process for the extraction of tetrahydro-β-naphthylamine is described. H. BURTON.

3-Nitrofluorene. F. E. BARDOUT (Anal. Asoc. Quím. Argentina, 1931, **19**, 117—136).—3-Nitro-2-aminofluorene (A., 1902, i, 758; 1928, 521) is converted on deamination (diazo-reaction and Cu_2O) into 3-*nitrofluorene*, m. p. 105°. Oxidation of the latter with K_2CrO_4 yields 3-nitrofluorenone, m. p. 232° (lit. 210°) [oxime, m. p. 217° (decomp.) (lit. 240°)], which is converted successively into the known 3-NH_2- and 3-OH-compounds. R. K. CALLOW.

Polycyclic aromatic hydrocarbons. VIII. Chemistry of 1 : 2 : 5 : 6-dibenzanthracene. J. W. COOK (J.C.S., 1931, 3273—3279; cf. A., 1931, 1420).—1 : 2 : 5 : 6-Dibenzanthracene (I) reacts additively with Br, pyridine dibromide, and maleic anhydride (but not with HNO_3 in AcOH), but more reluctantly than anthracene. These and other reactions recorded below show that angular *Bz* rings (in contrast to linear) stabilise the aromatic state of the *meso*-ring. (I) with Br in CS_2 at room temp. gives slowly a little additive compound (not isolated pure). With Br in pyridine (I) gives a salt which with aq. NH_3 gives 1 : 2 : 5 : 6-*dibenzanthronyl*-9-*pyridinium bromide*, m. p. indefinite. With HNO_3 (*d* 1·5) in AcOH (I) affords the 9-NO_2-compound, m. p. 217—218°, reduced by $NHPh\cdot NH_2$ (but not by $SnCl_2$ in AcOH) to 9-*amino*-1 : 2 : 5 : 6-*dibenzanthracene*, m. p. 268—269° (Ac_2 derivative, m. p. 215—216·5°; n-*butyryl* derivative, m. p. 300—302°; corresponding *succinimide*, m. p. 299—300°), which was oxidised by CrO_3 to 1 : 2 : 5 : 6-dibenzanthraquinone (whereby its constitution is proved). (I) and maleic anhydride at 250—260° give a product, hydrolysed by boiling NaOH to 1 : 2 : 5 : 6-*dibenzanthracene*-9 : 10-*endo*-αβ-*succinic acid*, m. p. 230° (Na_2 salt). 1 : 2 : 5 : 6-Dibenzanthraquinone with Sn and HCl in AcOH gives an insol. substance, but with Al and conc. H_2SO_4 gives 9-hydroxy-1 : 2 : 5 : 6-dibenzanthracene, isolated as *Ac* derivative, m. p. 235°, which led to the *Me ether*, m. p. 178°, unaffected by HCl in boiling AcOH. R. S. CAHN.

Molecular organic compounds. III. Molecular organic compounds of *o*-, *m*-, and *p*-monosubstituted nitrobenzenes. C. A. BUEHLER, C. R. ALEXANDER, and G. STRATTON (J. Amer. Chem. Soc., 1931, **53**, 4094—4096).—The following new mol. *compounds* (1 : 1 unless stated otherwise) are described: (*a*) *p*-nitrophenol and *o*-toluidine, m. p. 53·4° (all m. p. are corr.), benzidine, m. p. 149·9°, $NHEt_2$, m. p. 109·6°, and pyridine (2 : 1), m. p. 63·8°; (*b*) *m*-nitrophenol and *o*-toluidine, m. p. 40·6°, benzidine, m. p. 112·3°, and $NHEt_2$, m. p. 43°; (*c*) *o*-nitrophenol and $NHEt_2$, m. p. 105·1°, and (*d*) p-$C_6H_4Cl\cdot NO_2$ and α-naphthol, m. p. 165·2°. Other mol. compounds previously prepared by Kremann are also described with corr. m. p. The mol. compounds of high m. p. were prepared in EtOH, C_6H_6, or $CHCl_3$, whilst those with low m. p. were obtained by fusion of the components and subsequent heating at a fairly high temp. Differences in the ability of the nitrophenols to form mol. compounds are attributed to the chelate ring in the *o*-derivative. The comparatively high additive power of *m*- and p-$NO_2\cdot C_6H_4\cdot OH$ and their almost exclusive combination with NH_2-compounds indicate that in the simpler types union occurs between the OH and NH_2 groups. C. J. WEST (*b*).

***N*-Chlorosulphonamides and *N*-chlorosulphonylsulphonamides.** M. BATTEGAY, L. DENIVELLE, and J. MEYBECK (Compt. rend., 1931, **193**, 1195—1198).—N-(*Chlorosulphonyl*)-*formanilide*, m. p. 80—81°, -*acetanilide*, m. p. 75°, -p-*toluenesulphonanilide*, m. p. 139°, -p-*toluenesulphon*-o-*toluidide*, m. p. 108°, -p-*toluenesulphon*-m-*toluidide*, m. p. 126°, and -p-*toluenesulphon*-p-*toluidide*, m. p. 166°, are prepared by action of Na on the appropriate acylamide in dry Et_2O, and interaction of the resulting Na compound with SO_2Cl_2 at −5° to 0°. N-(*Chlorosulphonyl*)*benzanilide*, m. p. 109·5—110°, is better prepared by means of the Mg derivative obtained by action of MgPrCl on NHBzPh. H. A. PIGGOTT.

Chlorination of anilides. VII. Constitutional influence of acyl group on side-chain reactivity. G. WILLIAMS and S. P. HUGHES (J.C.S., 1931, 3125—3131; cf. A., 1928, 668).—The velocities of simultaneous *N*- and *C*-chlorination in 40% AcOH at 18° are measured in the NH_2Ph (CHO, Ac, and $CO\cdot CCl_3$ derivatives), *o*-chloroaniline (CHO, Ac, and $CO\cdot CH_2Cl$ derivatives), and *p*-chloroaniline series (CHO, Ac, CO·Et, $CO\cdot Pr^\alpha$, $CO\cdot Pr^\beta$, $CO\cdot CH_2Cl$, $CO\cdot CCl_3$, Bz, and $PhSO_2$ derivatives). Both are reduced by introduction of Cl or Ph into the acyl group, and the former also by increasing length or branching of the alkyl chain. Nuclear chlorination is favoured by the presence of Me in the acyl radical. The results are discussed in relation to the ionisation const. of the corresponding acids. H. A. PIGGOTT.

Inhibitory effects of substituents in chemical reactions. II. Reactivity of thiocarbimido-group in substituted arylthiocarbimides. D. W. BROWNE and G. M. DYSON (J.C.S., 1931, 3285—3308).—The velocities of interaction of phenylthiocarbimide and a large series of nuclear substituted derivatives with EtOH at its b. p. are measured by determination of unreacted thiocarbimide at definite time intervals by addition of benzidine, which reacts preferentially. In general, the velocity is increased by negative substituents and decreased by alkyl groups in any position; alkoxyl groups inhibit the reaction slightly in the *o*- and *p*-positions, and aid it in the *m*-position. The effects are additive in polysubstituted derivatives, and all the Me_3 compounds studied were unreactive. The following thiocarbimides, which appear to be new, are prepared from the appropriate amine and $CSCl_2$: 4-, m. p. 112°, and 3-*nitrophenyl*-, m. p. 60°; 3-*nitro*-o-*tolyl*-, m. p. 70°; 4-*fluoro*-3-*nitrophenyl*-, m. p. 55°; 4-*ethylphenyl*-, b. p. 245°; 4-iso*propylphenyl*-, b. p. 252°, 3-, b. p. 226—227°, and 4-*fluorophenyl*-, m. p. 12°, b. p. 228°; 3-, b. p. 269°, 4-, b. p. 268°, 5-, m. p. 36°, and 6-*chloro*-o-*tolyl*-, b. p. 276°; 4-, b. p. 272°, 5-, m. p. 34°, 2-, b. p. 264°, and 6-*chloro*-m-*tolyl*-, b. p. 270°; 2-*chloro*-p-*tolyl*-, b. p. 263°; 6-*chloro*-m-4-*xylyl*-, b. p. 278°; *chloromesityl*-, m. p. 44°; 3-*chloro*-p-*tolyl*-, b. p. 258°; 5-*chloro*-ψ-*cumyl*-6-, m. p. 36°; 3-*chloro*-p-*anisyl*-, m. p. 89°; 4-*chloro*-m-*anisyl*-, m. p. 51°; 5-*chloro*-o-*anisyl*-, m. p. 61°; 5-*chloro*-m-*anisyl*-, m. p. 36°; 3 : 5-*dimethoxyphenyl*-, m. p. 51°; p-*xenyl*-, m. p. 64°; and 4-, m. p. 71°; and 3-*aldehydophenyl-thiocarbimide*, m. p. 42°. 4-*Ethylphenyl*-, m. p. 138°; 4-iso*propyl*-, m. p. 134°; 3-*fluorophenyl*-, m. p. 116°; s-*di*-(3-*fluorophenyl*)-, m. p. 144°; s-*di*-(4-*fluorophenyl*)-, m. p. 145°; α-(5-*chloro*-o-*tolyl*)-β-(2-*naphthyl*)-, m. p. 163°; α-(6-*chloro*-m-*tolyl*)-β-(2-*naphthyl*)-, m. p. 154°; α-(6-*chloro*-o-*tolyl*)-β-(2-*naphthyl*)-, m. p. 150°; α-5-*chloro*-m-*tolyl*-β-p-*tolyl*-, m. p. 156°; α-3-*chloro*-o-*tolyl*-β-p-*tolyl*, m. p. 180°; 4-*chloro*-o-*tolyl*-, m. p. 138°; α-(2-*chloro*-p-*tolyl*)-β-(2-*naphthyl*)-, m. p. 149°; α-(6-*chloro*-m-4-*xylyl*)-β-(2-*naphthyl*)-, m. p. 154°; α-*chloromesityl*-β-(2-*naphthyl*-), m. p. 181°; α-(4-*chloro*-m-*tolyl*)-β-(2-*naphthyl*)-, m. p. 158°; α-(2-*chloro*-m-*tolyl*)-β-(2-*naphthyl*)-, m. p. 172°; α-3-*chloro*-p-*tolyl*-β-p-*tolyl*-, m. p. 160°; α-(5-*chloro*-6-ψ-*cumyl*)-β-(2-*naphthyl*)-, m. p. 161°; α-(3-*chloro*-p-*anisyl*)-β-(1-*naphthyl*)-, m. p. 174°; α-(4-*chloro*-m-*anisyl*)-β-(1-*naphthyl*)-, m. p. 155°; 5-*chloro*-o-*anisyl*-, m. p. 133°; α-(5-*chloro*-m-*anisyl*)-β-(p-*tolyl*)-, m. p. 136°; and α-3 : 5-*dimethoxyphenyl*-β-p-*tolyl*-, m. p. 148°, -*thiocarbamides* are described. By interaction of the appropriate thiocarbimide with EtOH: o-, m. p. 59°, m-, m. p. 115°, and p-*nitrophenyl*-, m. p. 175°; 2-*nitro*-m-*tolyl*-, m. p. 110°; 3-, m. p. 72°, and 2-*nitro*-p-*tolyl*-, m. p. 89°; 3-, m. p. 109°, 5-, m. p. 116°, and 4-*nitro*-o-*tolyl*-, m. p. 112°; 4-*nitro*-o-*anisyl*-, m. p. 76°; 3-*nitro*-4-*fluorophenyl*-, m. p. 118°; m-, m. p. 82°, and p-*chlorophenyl*-, m. p. 105°; 2 : 4-, m. p. 79°, 2 : 5-, m. p. 80°, and 3 : 5-*dichlorophenyl*-, m. p. 131°; m-, m. p. 84°, and p-*fluorophenyl*-, m. p. 86°; m-, m. p. 94°, and p-*bromophenyl*-, m. p. 107°; m-, m. p. 107°, and p-*iodophenyl*-, m. p. 98°; m-, m. p. 67°, and p-*tolyl*-, m. p. 85°; 3-o-*xylyl*-, m. p. 108°; p-*xylyl*-, m. p. 85°; and s-m-*xylyl*-, m. p. 88°; o-, m. p. 65°, m-, m. p. 85°, and p-*anisyl*-, m. p. 68°; 2 : 5-, m. p. 72°, 3 : 4-, m. p. 72°, and 3 : 5-*dimethoxyphenyl*-, m. p. 83°; m-, m. p. 75°, and p-*ethoxyphenyl*-, m. p. 95°; 2-*chloro*-m-*tolyl*-, m. p. 77°; 4-*chloro*-m-*tolyl*-, m. p. 59°; 6-*chloro*-o-*tolyl*-, m. p. 88°; 2-*chloro*-p-*tolyl*-, m. p. 88°; 5-*chloro*-m-*tolyl*-, m. p. 105°; 4-*chloro*-o-*tolyl*-, m. p. 81°; 5-*chloro*-o-*tolyl*-, m. p. 79°; 6-*chloro*-m-*tolyl*-, m. p. 101°; 6-*chloro*-4-m-*xylyl*-, m. p. 115°; 2-*chloro*-p-*anisyl*-, m. p. 96°; 5-*chloro*-m-*anisyl*-, m. p. 86°; 4-*chloro*-o-*anisyl*-, m. p. 81°; 6-*chloro*-m-*anisyl*-, m. p. 124°; 3-, m. p. 95°, and 4-*cyanophenyl*-, m. p. 110°; 3-, m. p. 147°, and 4-*aldehydophenyl*-, m. p. 135°; 4-*acetylphenyl*-, m. p. 111°; and 4-*xenyl*-, m. p. 117°, -*thiourethane*, NHR·CS·OEt, are prepared.

H. A. PIGGOTT.

Catalytic reduction of nitroanilines and *p*-phenylenediamine in presence of aldehydes and ketones. R. T. MAJOR (J. Amer. Chem. Soc., 1931, **53**, 4373—4378; cf. A., 1931, 837).—Catalytic reduction (Adams) of a mixture of *p*-NO_2·C_6H_4·NH_2 or *p*-$C_6H_4(NH_2)_2$ and $COMe_2$ at room temp. gives NN′-*di*iso*propyl*-p-*phenylenediamine*, m. p. 53° (*dihydrochloride*, decomp. when heated, obtained from the NN′-*dinitroso*-derivative, m. p. 110—111°, and conc. HCl; NN′-Bz_2 derivative, m. p. 180—181°; NN′-Ac_2 derivative, m. p. 180°). Similarly, *p*-NO_2·C_6H_4·NH_2 and COMeEt afford some *NN′*-di*sec*.-butylamino-*p*-phenylenediamine (*dihydrochloride*; *dinitroso*-derivative, m. p. 62°; Bz_2 derivative, m. p. 159—160°); with $COEt_2$, *NN′*-di-α-ethylpropyl-*p*-phenylenediamine (*dinitroso*-derivative, m. p. 96°; Bz_2 derivative, m. p. 132°) results. In all these reductions some *p*-phenylenediamine is produced. Benzoylation of the reduction product from *m*-NO_2·C_6H_4·NH_2 and $COMe_2$ gives only *NN′*-dibenzoyl-*m*-phenylenediamine. *o*-NO_2·C_6H_4·NH_2 and $COMe_2$ afford (after benzoylation) N-*benzoyl*-NN′-*di*iso*propyl*-, m. p. 147—148°, and N-*benzoyl*-N′-iso*propyl*-, m. p. 159—160°, -o-*phenylenediamine* (5% yield of each) in addition to *NN′*-dibenzoyl-*o*-phenylenediamine. Reduction of a mixture of *p*-NO_2·C_6H_4·NH_2 and PhCHO gives 50% of tetrabenzyl-*p*-phenylenediamine.

C. J. WEST (*b*).

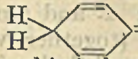
Nitroamines. II. Nitrophenylnitroamines. E. MACCIOTTA (Gazzetta, 1931, **61**, 773—777).—3 : 5-, 2 : 3-, and 3 : 4-dinitroanilines with HNO_3 and Ac_2O (J.C.S., 1902, **81**, 806) give respectively 3 : 5-, isolated only as *Hg* salt, $[C_6H_3(NO_2)_2\cdot N{:}NO_2]_2Hg$, 2 : 3-, and 3 : 4-*dinitrophenylnitroamines*. 2 : 3- and 3 : 4-Dinitroanilines with HNO_3 and H_2SO_4 give 2 : 3 : 4 : 6-tetranitrophenylnitroamine, m. p. 105° (decomp.). 3 : 5-Dinitroaniline gives an unstable *compound*, probably penta-substituted. E. E. J. MARLER.

Preparation and resolution of α-phenylethylamine. E. ANDRÉ and C. VERNIER (Compt. rend., 1931, **193**, 1192—1194).—*dl*-α-Phenylethylamine is obtained in 70% yield by hydrolysis of the cryst. *ammonium bromide* from α-phenylethyl bromide and hexamethylenetetramine with HCl in EtOH at 95°. It is conveniently resolved into optically active forms by *l*-quinic and *d*-tartaric acids. H. A. Piggott.

Nitroamines. III. *m*-Phenylenedinitroamine. E. Macciotta (Gazzetta, 1931, 61, 777—782).—*m*-Phenylenediamine with $EtNO_3$ and a solution of K in EtOH and Et_2O or with HNO_3 and Ac_2O gives m-*phenylenedinitroamine* (*K_2*, *Ag_2*, *Pb* salts). *m*-Phenylenediamine nitrate with $AlCl_3$ (A., 1902, i, 312) gives only *m*-phenylenediamine hydrochloride. E. E. J. Marler.

Complex compounds of cobalt with *s*-diphenylethylenediamine. J. V. Dubsky and A. Langer (Publ. Fac. Sci. Univ. Masaryk, 1931, No. 145, 1—8).—The products described by Gapon (A., 1930, 765) are not compounds but mixtures of diphenylethylenediamine hydrochloride with $CoCl_2$ or with the double salt of these two substances. R. Truszkowski.

Reactions of azoxy- and azo-compounds with benzyl alcohol, benzaldehyde, and quinoline. W. M. Cumming and G. Howie (J.C.S., 1931, 3181—3185).—Azoxybenzene (I) and *p*-azoxytoluene are reduced by boiling $CH_2Ph{\cdot}OH$ in CO_2 to azobenzene (II) and *p*-azotoluene, respectively. Similarly, (I) and PhCHO give about 10% of NHBzPh, formed in almost quant. yield from (II) and PhCHO, whilst *p*-azotoluene is converted into benz-*p*-toluidide. Benzoin is not a factor in the second set of reactions, but (II) is reduced by benzoin in absence or presence of $CH_2Ph{\cdot}OH$ to NH_2Ph. Reaction between (II) and PhCHO may occur thus: $2PhCHO+(:NPh)_2\longrightarrow[Ph{\cdot}C(OH){:}NPh]_2\longrightarrow 2NHBzPh$. *s*-1 : 1′-Azoxynaphthalene (III) is not reduced by $CH_2Ph{\cdot}OH$ or PhCHO, but is converted into the *as*-form (IV) (J.C.S., 1923, 123, 2464). 1 : 1′- and 2 : 2′-Azonaphthalenes do not react with PhCHO. (III), PhCHO, and quinoline at 170° give (IV) and 33% of 2-*hydroxy*-1 : 1′-*azonaphthalene* (V), m. p. 230°, also prepared by coupling α-naphthylamine and β-naphthol. (V) and not the 4-hydroxyazo-compound [as suggested by Baudisch and Fürst (A., 1913, ii, 38)] is also formed when (III) [or (IV)] is exposed to light; the hydroxyazo-compound, m. p. 224°, of Cumming and Steele (cf. A., 1926, 162) is (V). The reaction between PhCHO and (I) or (II) is inhibited by quinoline. A basic condensation product, m. p. 99—100°, of PhCHO and quinoline is formed when the reactants are heated. H. Burton.

Hydrolysis of salts of hydrazo-compounds. B. P. Orelkin, A. T. Ryskaltschuk, and M. A. Aizikovitsch (J. Gen. Chem. Russ., 1931, 1, 696—703).—Treatment of hydrazobenzene hydrochloride, prepared in Et_2O solution, with H_2O gives 30% of benzidine, 60% of diphenyline and semidine, and 10% of hydrazobenzene (with some azobenzene); keeping the solution for 24 hr. before hydrolysis increases the benzidine and diphenyline fractions at the expense of the hydrazobenzene. Rapid saturation of ethereal hydrazobenzene with HCl, followed by hydrolysis, gives 46% of benzidine, 14% of diphenyline, and 40% of hydrazobenzene, no semidine being formed. Solid hydrazobenzene with HCl below —20° forms an emerald-green *dihydrochloride*, yielding 21% of benzidine, 56% of diphenyline and semidine, and 23% of hydrazobenzene on hydrolysis. The green salt is formulated as =NHCl·NHPh,HCl, and it is assumed that this is hydrolysed to NHPhCl and NH_2Ph, which then combine to form semidine. The formation of NHPhCl cannot take place when 1 mol. of HCl is added to the base, as assumed by Franzen and von Fürst (A., 1917, i, 58), because no semidine is formed unless the reaction product is kept. Hydrolysis of the green salt with aq. NH_3 gives $NHPh{\cdot}NH_2$, confirming the formation of intermediate products suggested; the yield of benzidine is reduced. *o*-Hydrazotoluene forms a green *dihydrochloride* at —50°, yielding *o*-tolidine and *o*-semidine, but no *p*-semidine, on hydrolysis. *p*-Hydrazotoluene forms a brownish-red dihydrochloride, hydrolysed to the appropriate *o*-semidine. *o*- and *p*-Hydrazoanisole form unstable violet *dihydrochlorides*; violet dihydrochlorides are also obtained from *o*- and *p*-azoanisoles (m. p. 149° and 120°), but these readily lose HCl, re-forming the base. G. A. R. Kon.

Oxidising properties of normal diazonium hydroxides. Z. Jolles (Atti R. Accad. Lincei, 1931, [vi], 14, 115—119).—A brief summary of published work. T. H. Pope.

Diazo-compounds sensitive to light. III. *p*-Substituted diazo- and tetrazo-compounds. J. Schmidt and W. Maier (J. pr. Chem., 1931, [ii], 132, 153—162; cf. A., 1931, 752).—Complex *salts* of the following diazonium chlorides with the components named are described: *p*-diazodimethylaniline $+HgCl_2$, m. p. 160° (decomp.), $+FeCl_3$, m. p. 109° (decomp.); *p*-diazodiethylaniline $+HgCl_2$, m. p. 119° (decomp.), $+FeCl_3$; *p*-diazodiphenylamine $+HgCl_2$, m. p. 144° (decomp.), $+0{\cdot}5ZnCl_2$, m. p. 141°, $+0{\cdot}5CdCl_2$; *pp*′-tetrazodiphenyl $+2HgCl_2$, $+ZnCl_2$, $+2CdCl_2$. The following substances do not yield similar complex salts: 2 : 6-dibromodiazobenzene-4-sulphonic acid (I) (dimorphous crystals of the internal betaine), 3 : 5-dichloro-4-diazophenetole, 3 : 5-dichloro-4-azophenol, *pp*′-tetrazodiphenylmethane. The above diazo-compounds (except the last-mentioned) are stable in the dark, but sensitive to light. (I) couples with phenols even in acid solution, but not with amines. R. S. Cahn.

Diazo-compounds. IV. H. T. Bucherer and G. von der Recke (J. pr. Chem., 1931, [ii], 132, 113—144; cf. A., 1931, 1409—1410).—Previous work (*loc. cit.*) on the action of CO_2 and other weak acids on *anti*diazotates is confirmed, and similar results are obtained with diazotised *o*-nitroaniline, *p*-nitro-*o*-anisidine, and *p*-chloro-*o*-nitroaniline. The formation of the diazoamino-compound (the yield of which varies with the experimental conditions) is considered to be due to change of the *anti*diazotate into diazonium hydroxide (? carbonate), which hydrolyses to the amine and HNO_2, the amine subsequently coupling with more diazonium hydroxide. HNO_2 replaces the N_2Cl group in diazonium salts by NO_2 slowly at 0° and more rapidly at temp. up to 50°, the yields varying according to the amounts of HNO_2 and HCl used; the max. yields of pure NO_2-compound for the bases named were as follows: *o*-, *m*-, and *p*-nitroaniline, 58, 30, and 50%, respectively; *p*-chloroaniline, 23%; α- and β-naphthylamine, 4 and 5·5%, respectively (together with the naphthols); sulphanilic acid, α-naphthylamine-4- and-5-sulphonic acid, 0%; benzidine, 8%. Diazotised *p*-chloroaniline and HCN give additive *compounds*, m. p. 178°, 69°, and 103°, and much tar. The compound, m. p. 103°, gives HCN and tar with H_2SO_4 in AcOH, and NH_4Cl with HCl in EtOH; it condenses with CH_2O, MeCHO, and PhCHO in EtOH or AcOH; CH_2O leads to a *substance*, $C_{17}H_{10}N_6Cl_2$, m. p. 135°, hydrolysed by conc. H_2SO_4 at 125—135° to a *substance*, m. p. 201°. *p*-Nitroaniline gives a similar *compound*, m. p. 126°, which with CH_2O, MeCHO, and PhCHO gives *substances*, m. p. 195°, 144°, and 193°, respectively. Diazotised β-naphthylamine and HCN give naphthalene-β-*anti*diazocyanide, which does not react with aldehydes. Aq. Na phenylhydrazinesulphonate reacts only after 25—30 min. with PhCHO to form benzaldehydephenylhydrazone, hydrolysis of the sulphonate being slow at first, but later catalysed by the acid formed. CH_2O reacts after 1·5 hr., but the product could not be purified. R. S. CAHN.

Action of hydrogenating and mixed catalysts on the cracking of phenols with hydrogen. A. KLING and D. FLORENTIN (Compt. rend., 1931, **193**, 1023—1024).—A study of the action of various catalysts on mixtures of PhOH and H_2 at 470—490° and approx. 300 kg. per sq. cm. The products are identified by determinations of b. p., *d*, and *n*. NiO or Mo_2O_5 with excess of H_2 give mainly C_6H_6 and *cyclo*hexane; with insufficient H_2 the latter catalyst gives heavier hydrocarbons, and conversion is incomplete. Mo_2O_3 activated by heating at 500° induces dehydration rather than hydrogenation even when H_2 is in excess. Dehydrating catalysts, however, activated by heat and addition of 5—10% Mo_2O_5, cause rapid and complete transformation of PhOH into hydrocarbons rich in C_6H_6, even with an excess of H_2.

H. A. PIGGOTT.

Rearrangement of hydroxy-sulphones. I. A. A. LEVY, H. C. RAINS, and S. SMILES (J.C.S., 1931, 3264—3269).—Further examples are given in support of the mechanism assigned to the rearrangement of β-naphthol-1-sulphone (A., 1931, 1153). Interaction of 2-nitrophenylchlorothiol with *p*-cresol in $CHCl_3$ gives 2-*nitrophenyl* 4-*hydroxy*-m-*tolyl sulphide*, m. p. 146—147° (*Ac* derivative, m. p. 106°), which is oxidised by H_2O_2 in AcOH to the corresponding *sulphone*, m. p. 140—141°; this in presence of alkali (1 mol. or more) rearranges into 2-*nitrophenol* 3-*sulphino*-p-*tolyl ether*, m. p. 132—133°, which is reduced by aq. HI in AcOH to 4-o-*nitrophenoxy*-m-*tolyl disulphide*, m. p. 117°, and on oxidation with alkaline $KMnO_4$ and hydrolysis of the resulting sulphonic acid with 60% H_2SO_4 gives *o*-nitrophenyl *p*-tolyl ether. 2-*Nitrophenyl* 2-*hydroxy*-1-*naphthyl sulphone*, m. p. 181°, obtained by oxidation of the Ac derivative of the corresponding sulphide and hydrolysis of the resulting *Ac* derivative, m. p. 152—153°, with 10% H_2SO_4 in EtOH, passes rather more rapidly into 2-*nitrophenyl* 1-*sulphino*-β-*naphthyl ether*, m. p. 118°, in alkaline solution. This sulphinic acid, which is more readily prepared by hydrolysis of the acetylsulphone with NaOH in EtOH, gives a *Me* ester, m. p. 141°, with a large excess of Me_2SO_4 and aq. NaOH, and is converted as in the preceding case into 2-o-*nitrophenoxy*-1-*naphthyl disulphide*, m. p. 207° (identified by further reduction with glucose and NaOH to the sulphide), and o-*nitrophenyl* β-*naphthyl ether*, m. p. 58°. The last-named is also obtained by interaction of Na β-naphthoxide and *o*-chloronitrobenzene in EtOH. H. A. PIGGOTT.

Simplified preparation of organic compounds. V. 4-Nitropyrocatechol. H. VAN ERP (Ber., 1931, **64**, [*B*], 2813—2815).—2-Chloro-4-nitrophenol, KOH, and H_2O are warmed on the water-bath until a uniform paste of the phenoxide is produced, which is subsequently heated over a free flame until orange and red materials have disappeared and the odour of NH_3 is distinct. The 4-nitropyrocatechol, m. p. 174—174·5° (corr.), is purified through the *Ba* salt ($+3H_2O$). The Ac_2, m. p. 78° (corr.) and Bz_2, m. p. 157·5° (corr.), derivatives are described. Substitution of NaOH for KOH leads to complete decomp. of 2-chloro-4-nitrophenol. H. WREN.

Reputed dehydrogenation of quinol by palladium-black. L. J. GILLESPIE and T. H. LIU (J. Amer. Chem. Soc., 1931, **53**, 3969—3972).—The dehydrogenation of quinol by Pd reported by Wieland (A., 1912, i, 247) was not observed when precautions were taken to exclude traces of Pd hydroxide.

H. F. JOHNSTONE (*b*).

Rates of formation of the stereomeric methyl*cyclo*hexanols. A. SKITA and W. FAUST (Ber., 1931, **64**, [*B*], 2878—2892).—2-Methyl*cyclo*hexanone, when hydrogenated at 70°/3 atm. in AcOH in presence of colloidal Pt, is converted into *cis*-2-methyl*cyclo*hexanol, b. p. 165° (corr.)/760 mm., d_4^{18} 0·9356 (3 : 5-*dinitrobenzoyl* derivative, m. p. 98—99°; phenylurethane, m. p. 90—91°). When similarly but more slowly reduced, a mixture of about 75% of *cis*- and 25% of *trans*-2-methyl*cyclo*hexanol results. Diminution of the rate of hydrogenation by reduction of temp. or pressure of H_2 causes further increase in the proportion of *trans*- to *cis*-alcohol. In almost neutral solution the product contains 35% of the *cis*-modification. In presence of *cyclo*hexylamine reduction proceeds more rapidly than in neutral solution and affords about 50% of *cis*-2-methyl*cyclo*hexanol; as by-products, di*cyclo*hexylamine (hydrochloride, m. p. 327°), cyclo*hexyl*-2-*methyl*cyclo*hexylamine*, b. p. 128—129°/17 mm., d_4^{18} 0·9124 (*hydrochloride*, m. p. 258—259°; *picrate*, m. p. 149°), and a *base*, $C_{13}H_{25}N$, b. p. 128—129°/16 mm., d_4^{18} 0·9095 (*picrate*, m. p. 157—158°), are obtained.

Technical 2-methyl*cyclo*hexanol (from *o*-cresol according to Sabatier) is converted into the 3 : 5-dinitrobenzoate, m. p. 114—115°, which with NaOH in H_2O–MeOH yields homogeneous *trans*-2-methyl*cyclo*hexanol, b. p. 166·5° (corr.)/760 mm., $d_4^{19\cdot7}$ 0·9241 (phenylurethane, m. p. 105—106°). Purification of the technical product through the H phthalate, m. p. 123·5—125°, is described. Reduction of 2-methyl*cyclo*hexanone by Na in moist Et_2O leads to the *trans*-alcohol, whilst slow hydrogenation of *o*-cresol at room temp. in presence of colloidal Pt gives methyl*cyclo*hexane and a carbinol mixture containing 60% of the *cis*-isomeride.

Rapid hydrogenation of 3-methyl*cyclo*hexanone and treatment of the product with 3 : 5-dinitrobenzoyl chloride leads to the isolation of *cis*-3-methyl*cyclo*hexanol, b. p. 173—174° (corr.)/760 mm., $d_4^{21\cdot8}$ 0·9173 (3 : 5-*dinitrobenzoate*, m. p. 91—92°; phenylurethane, m. p. 87—88°). Reduction of the *cyclo*hexanone with Na in moist Et_2O and subsequent treatment with 3 : 5-dinitrobenzoyl chloride affords *trans*-3-methyl*cyclo*hexanol, b. p. 174—175°/(corr.)/762 mm., d_4^{20} 0·9145 (3 : 5-*dinitrobenzoate*, m. p. 97—98°; phenylurethane, m. p. 93—94°).

Rapid catalytic reduction of 4-methyl*cyclo*hexanone permits the isolation of *cis*-4-methyl*cyclo*hexanol, b. p. 173—174°/ (corr.)/750 mm. (3 : 5-*dinitrobenzoate*, m. p. 134°; phenylurethane, m. p. 118—119°), whilst reduction by Na in moist Et_2O leads to *trans*-4-methyl*cyclo*hexanol, b. p. 173—174·5° (corr.)/745 mm., $d_4^{20\cdot7}$ 0·9118 (3 : 5-*dinitrobenzoate*, m. p. 139—140°; phenylurethane, m. p. 124—125°). Particularly in the cases of the 3- and 4-methyl*cyclo*hexanols the differences in the vals. of *d* and *n* for the isomerides are very small and the determination of the heat of combustion is advocated.

It is established that in general the modification richer in energy is formed to a greater extent as the rate of hydrogenation is increased when the possibility exists of converting an unsaturated cyclic compound into stereoisomeric substances by addition of H_2.

H. WREN.

cis- and *trans*-2-Methyl*cyclo*hexanol. W. HÜCKEL and K. HAGENGUTH (Ber., 1931, **64**, [*B*], 2892—2895).—Technical 2-methyl*cyclo*hexanol when purified through the H phthalate, m. p. 124—125°, yields homogeneous *trans*-2-methyl*cyclo*hexanol, m. p. —21·2° to —20·5°, b. p. 167·2—167·6°/760·1 mm., d_4^{19} 0·9245 (p-*nitrobenzoate*, m. p. 65°; oxalate, m. p. 61°), oxidised by CrO_3 in AcOH to 2-methyl*cyclo*hexanone (oxime, m. p. 43—44°). Hydrogenation of *o*-cresol at 20°/3 atm. in presence of colloidal Pt and aq. HCl affords 30% of methyl*cyclo*hexane and 70% of methyl*cyclo*hexanol containing a little methyl*cyclo*hexanone. The alcohol is purified through the p-*nitrobenzoate*, m. p. 51—52°. *trans*-2-Methyl*cyclo*hexyl *p*-toluenesulphonate, m. p. 27—28°, is converted by anhyd. KOAc in EtOH into AcOEt, Δ^1-methyl*cyclo*hexene, Et methyl*cyclo*hexyl ether, and methyl*cyclo*hexyl acetate, b. p. 64·2—65·4°/10 mm. Hydrolysis of the acetate and purification of the alcohol through the *p*-nitrobenzoate or H phthalate, m. p. 104°, leads to homogeneous *cis*-2-methyl*cyclo*hexanol, m. p. —9·5° to —9·2°, b. p. 165·2—165·4°/761·2 mm., $d_4^{15\cdot9}$ 0·9381 (phenylurethane, m. p. 92°).

H. WREN.

Amino-alcohols. VII. Phenolic arylpropanolamines. W. H. HARTUNG, J. C. MUNCH, E. MILLER, and F. CROSSLEY (J. Amer. Chem. Soc., 1931, **53**, 4149—4160; cf. A., 1931, 834).—A study of the physiological activity of the compounds now described shows that the *p*-OH group increases pressor activity and decreases toxicity to rabbits; the *m*-OH group increases activity at least twice as much as does the *p*-isomeride and also increases toxicity; the *o*-OH group decreases the activity and probably increases toxicity; the *mp*-$(OH)_2$ group is the most active and produces an action resembling that of adrenaline. It is not safe to predict the toxicity of a compound obtained by the introduction, simultaneously, of more than 1 group. The following *oximino-ketones*, $Ar\cdot CO\cdot CMe{:}NOH$, are prepared in 25—90% yield, where $Ar{=}p$-$OH\cdot C_6H_4$, m. p. 184·5° (all m. p. are corr.); *m*-$OH\cdot C_6H_4$, m. p. 138°; *mp*-$Me(OH)C_6H_3$, m. p. 188·5—189°; *pm*-$Me(OH)C_6H_3$, m. p. 158·5°; *mp*-$(OH)_2C_6H_3$, m. p. 217° (decomp.); *p*-$MeO\cdot C_6H_4$, m. p. 131°; *o*-$MeO\cdot C_6H_4$, m. p. 132°; *op*-$(MeO)_2C_6H_3$, m. p. 110·5°. Catalytic reduction gives the corresponding *amino-ketones*, $Ar\cdot CO\cdot CHMe\cdot NH_2$, analysed as the *hydrochlorides*, where $Ar{=}p$-$OH\cdot C_6H_4$, m. p. 219°; *m*-$OH\cdot C_6H_4$, m. p. 177°; *mp*-$Me(OH)C_6H_3$, m. p. 184·5°; *pm*-$Me(OH)C_6H_3$, m. p. 145°; *mp*-$(OH)_2C_6H_3$, m. p. 233°; *p*-$MeO\cdot C_6H_4$, m. p. 226°; *o*-$MeO\cdot C_6H_4$, m. p. 112°; *op*-$(MeO)_2C_6H_3$, m. p. 178—180°. Further catalytic reduction gives the *amino-alcohols*, $Ar\cdot CH(OH)\cdot CHMe\cdot NH_2$, analysed as the *hydrochlorides*, where $Ar{=}p$-$OH\cdot C_6H_4$, m. p. 203·5°; *m*-$OH\cdot C_6H_4$, m. p. 182°; *mp*-$Me(OH)C_6H_3$, very hygroscopic; *pm*-$Me(OH)C_6H_3$, m. p. 222°; *mp*-$(OH)_2C_6H_3$, m. p. 176°; *p*-$MeO\cdot C_6H_4$, m. p. 216·5°; *o*-$MeO\cdot C_6H_4$, m. p. 245° (decomp.) (free *base*, m. p. 75°); *op*-$(MeO)_2C_6H_3$, m. p. 219°. o-*Hydroxyphenyl α-aminoethyl ketone*, from the MeO derivative and conc. HCl, gives a *hydrochloride*, m. p. 223·5—224°; the reduction product was not obtained pure. 2 : 4-*Dihydroxyphenyl α-aminoethyl ketone hydrochloride*, m. p. 176°, 2 : 4-*dihydroxyphenylpropanolamine hydrochloride*, m. p. 249°, and o-*propionylphenoloxime*, m. p. 94°, are described. Data for the min. lethal dose and relative pressor activity of the amino-alcohol hydrochlorides are given.

C. J. WEST (*b*).

Reaction between phenylcarbimide and ω-anilinophenyl-β-hydroxynaphthylmethanes. II. A. NERI (Gazzetta, 1931, **61**, 815—819).—ω-Anilino-*m*-nitrophenyl-2-hydroxy-1-naphthylmethane reacts with PhNCO to give *diphenyl*-(m-*nitrophenyl-2-hydroxy*-1-*naphthylmethyl*)*carbamide*, $NHPh\cdot CO\cdot NPh\cdot CH(C_6H_4\cdot NO_2)\cdot C_{10}H_6\cdot OH$, m. p. 143°, which when boiled with HCl gives *s*-diphenylcarbamide and *m*-nitrophenyldi-(2-hydroxy-1-naphthyl)-methane; *m*-nitrobenzaldehyde is probably present, but was not isolated. ω-Anilinophenyl-1-hydroxy-2-naphthylmethane with PhNCO gives only *s*-diphenylcarbamide, PhCHO, and phenyldi-(1-hydroxy-2-naphthyl)methane.

E. E. J. MARLER.

Condensations by sodium instead of by the Grignard reaction. III. *tert*.-Carbinols and acids. A. A. MORTON and J. R. STEVENS (J. Amer. Chem. Soc., 1931, **53**, 4028—4032).—$Ph\cdot C_6H_4Cl$ (0·1 mol.), Et_2CO_3 (0·042 mol.), and Na wire (0·22 g.) in C_6H_6 (100 c.c.) heated for 10 hr. give 23% of $(Ph\cdot C_6H_4)_3C\cdot OH$, m. p. 207°. Similarly, PhCl affords 66% of $CPh_3\cdot OH$; PhCl, BzCl, and Na give 79% of $CPh_3\cdot OH$, whilst $COPh_2$ affords 98%; PhCl, BzOEt, and Na in NEt_2Ph yield 62% of $CPh_3\cdot OH$. *p*-$C_6H_4Cl\cdot NMe_2$, Et_2CO_3, and Na give 22% of crystal-violet (formed in 49% yield using *p*-$C_6H_4Br\cdot NMe_2$), also obtained in 40% yield using $ClCO_2Et$ for Et_2CO_3.

Malachite-green (69% yield) is prepared from p-$C_6H_4Br{\cdot}NMe_2$, BzOEt, and Na. $Ph{\cdot}C_6H_4Cl$, BzOEt, and Na in absence of solvent give 7·3% of phenyldi-(diphenylyl)carbinol; in presence of C_6H_6 the yield is only 1%. 1-$C_{10}H_7Cl$, Ph diphenylyl ketone, and Na in Et_2O afford 7·4% of phenyldiphenylylnaphthylcarbinol, whilst $(CH_2Ph)_3C{\cdot}OH$ is obtained from CH_2PhCl, Et_2CO_3, and Na in C_6H_6. The following acids were prepared from the requisite aryl chloride, CO_2 (30 lb. pressure), and Na in C_6H_6: m- (58%) and p-toluic (76%), BzOH (45%), p-$NMe_2{\cdot}C_6H_4{\cdot}CO_2H$ (28%), and p-$Ph{\cdot}C_6H_4{\cdot}CO_2H$ (12%). Caution is necessary in carrying out these experiments, since the reaction proceeds with explosive violence when it gets beyond control. The formation and methods of removal of a film on the surface of Na are discussed.

C. J. West (*b*).

[Tetraphenyl-*o*-xylylene.] E. de B. Barnett and J. W. Cook (Ber., 1931, 64, [*B*], 2936; cf. Wittig and Leo, A., 1931, 1405).—The identity of 1-hydroxydiphenylmethyl-2-benzhydrylbenzene has been established previously by the authors. H. Wren.

[Conjugated double linkings. XX. Perkin's synthesis.] P. Kalnin (Ber., 1931, 64, [*B*], 2935). —A comment on the communication of Kuhn and Ishikawa (A., 1931, 1413). H. Wren.

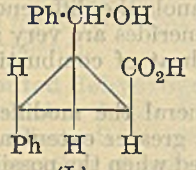
Scission of β-hydroxy-substituted acids. Preparation of deoxybenzoins. D. Ivanov and J. Popov (Bull. Soc. chim., 1931, [iv], 49, 1547—1551).—When heated with 10% aq. NaOH for 0·5 hr., triaryl-β-hydroxybutyric acids previously described (A., 1931, 726) are decomposed into phenylacetic acids and deoxybenzoins. When the OH group is attached directly to the ring, *e.g.*, in phenyl-1-hydroxy*cyclo*hexylacetic acid, a longer heating is required, *e.g.*, 5½ hr. The following ketones are described: p-*bromophenyl benzyl ketone*, m. p. 113·5—115° (from β-*hydroxy-αγ-diphenyl*-β-p-*bromophenylbutyric acid*, m. p. 172·5—173·5°, obtained in 81% yield from CH_2PhCl, $CH_2Ph{\cdot}CO_2{\cdot}MgCl$, and Mg p-bromophenyl bromide); m-*tolyl* p-*chlorobenzyl ketone*, m. p. 88—89°; p-*tolyl* p-*chlorobenzyl ketone*, m. p. 112·5—114°; and p-*bromophenyl* p-*chlorobenzyl ketone*, m. p. 126—127°.

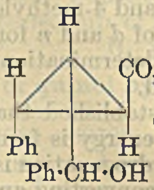
R. Brightman.

Manufacture of arylamides of aromatic hydroxycarboxylic acids [hydroxydiphenylaminecarboxylic acids]. W. W. Groves. From I. G. Farbenind. A.-G.—See B., 1932, 57.

Isomeric α-phenyl-β-*p*-tolyl-δ-ketonic acids. S. Avery and M. J. Hall (J. Amer. Chem. Soc., 1931, 53, 4350—4353; cf. A., 1930, 1433).—Fractional crystallisation of crude γ-trimethylacetyl-αβ-diphenylbutyric acid (cf. *loc. cit.*) from dil. EtOH gives a form, m. p. 179—180° (ratio to less fusible acid, 1 : 10); no cryst. alkaloidal salt could be obtained from either form. Condensation of Ph p-methylstyryl ketone with derivatives of $CH_2Ph{\cdot}CO_2H$ using NaOMe or NaOEt gave *γ-benzoyl-α-phenyl*-β-p-*tolylbutyric acid*, m. p. 250—251° (*Me* ester, m. p. 162°; *Et* ester, m. p. 145—146°; *nitrile*, m. p. 130°; *lactone*, m. p. 187—188°); an isomeride of the acid could not be isolated. p-*Methylstyryl* tert.-*butyl ketone*, m. p. 83·4° (25% yield from p-$MeC_6H_4{\cdot}CHO$ and CMe_3Ac) gave the following compounds: *γ-trimethylacetyl-α-phenyl*-β-p-*tolylbutyric acid*, m. p. 215—216° and 198—199° [*Me* ester, m. p. 139—140°; *Et* ester, m. p. 132—133°; *nitrile*, m. p. 128—129° (corresponds with the more fusible acid)]. C. J. West (*b*).

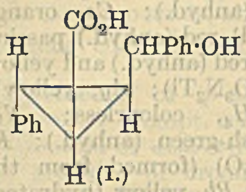
Degradation of α-truxillic acid. XV. Action of nitrosyl bromide on γ-amino-acids. R. Stoermer and W. Keller (Ber., 1931, 64, [*B*], 2783—2792; cf. A., 1928, 174; 1929, 64).—α-Truxillyl chloride is treated with Na truxillate in boiling C_6H_6 or xylene and subsequently with NH_3, thus yielding a mixture of the α-acid, its mono- and di-amide. Treatment of the mixed acids with NaOCl leads to the isolation of "*α-truxillamic* [3^t-*amino*-2^t : 4^c-*diphenyl*cyclo*butane*-1^c-*carboxylic*] *acid* (+3H_2O), m. p. 212° (decomp.) [*hydrochloride*, m. p. 280° (decomp.); *Me* ester, m. p. 73°; *Ac* derivative, m. p. 248°]. It is converted by NOBr in Et_2O into αδ-diphenylbutadiene, the phenyl-α-hydroxybenzyl*cyclo*propanecarboxylic acids (I), m. p. 168° (decomp.), and (II), m. p. 186°, and *α-α′-hydroxybenzyl*-β-*benzylidenepropionic* [*α-hydroxy-αδ-diphenyl*-Δ^γ-*butene*-β-*carboxylic*] *acid*, m. p. 148—149°. The last-named acid loses PhCHO when treated with alkali; this property is not shared by the *Me* ester, m. p. 92—93°. It is more conveniently prepared by the action of AcOH and H_2SO_4 on the acid (II) followed by hydrolysis. Acetylation of the acid appears impossible owing to ready loss of H_2O with formation of αβ-dibenzylidenepropionic acid, m. p. 168°. Catalytic hydrogenation (Pd–$BaSO_4$) gives γ-phenyl-α-α′-hydroxybenzylbutyric acid. α-α′-Hydroxybenzyl-β-benzylidenepropionic acid is converted by Br in $CHCl_3$ into a compound, m. p. 155—170°, transformed by Ac_2O and NaOAc into γ-phenyl-α-benzylidene*iso*crotonolactone, m. p. 152°. With HBr in Et_2O the unsaturated acid gives *α-α′-bromobenzyl*-β-*benzylidenepropionic acid*, m. p. 167° (decomp.) (*Me* ester, m. p. 118—119°), obtained also from the acids (I) and (II); with AcOH, H_2O, and H_2SO_4 it yields αδ-diphenylbutadiene and α-α′-hydroxybenzyl-β-benzylidenepropionic acid. With HCl the unsaturated acid does not appear to react, whereas its Ac derivative smoothly yields α-α′-chlorobenzyl-β-benzylidenepropionic acid, m. p. 156°. The Me ester of the OH-acid is transformed by $SOCl_2$ and pyridine in Et_2O into Me α-α′-chlorobenzyl-β-benzylidenepropionate, m. p. 97°. H. Wren.


(I.)

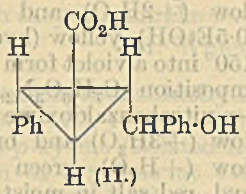

(II.)

Degradation of δ-truxinic acid. XVI. R. Stoermer and E. Asbrand (Ber., 1931, 64, [*B*], 2793—2796).—δ-Truxinic acid in C_6H_6 is treated with $SOCl_2$ (whereby slight isomerisation to the ζ-acid occurs) and subsequently with NH_3. Semi-hydrolysis of the diamide affords *δ-truxinamic acid* (+3H_2O), m. p. 198° (decomp.) [*hydrochloride*, m. p. 198°; *Me* ester, m. p. 126° (decomp.), and its *hydrochloride*,

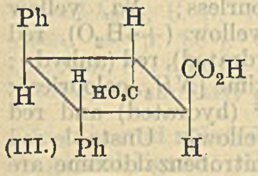
m. p. 188°. *Ac* derivative, m. p. 228°, and its *Me* ester, m. p. 105°]. The amic acid is converted by NOBr in Et_2O into αδ-diphenylbutadiene and its tetrabromide, the lactone of the OH-acid (I), the *trans*-OH-acid (II), and an acid, m. p. about 132°, which loses PhCHO when treated with alkali and is identical with or closely related to α-α′-hydroxybenzyl-β-benzylidene-propionic acid. The configuration (III) for δ-truxinic acid is established.



(I.)



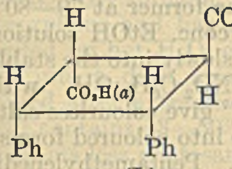
(II.)



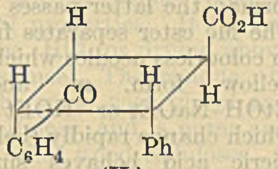
(III.)

H. WREN.

***neo*Truxinic acid. XVI.** R. STOERMER and E. ASBRAND (Ber., 1931, **64**, [*B*], 2796—2804).—β-Truxinic acid is treated with H_2O at 215—220°, the product is extracted with 5% EtOH and purified through the NH_2 salt, whereby *neo*truxinic acid is obtained in 25% yield. It is converted by $SOCl_2$ in C_6H_6 and then by NH_3 into *neo*truxindiamide, m. p. 249°, which yields β-truxinamic acid, m. p. 194·5° (decomp.), when treated with 1 mol. of KOH in EtOH, and a mixture of the β-amic acid and neo*truxin*-a-*amic acid* (cf. I), m. p. 214°, under the action of 5 mols. of KOH. The last-named acid is conveniently prepared from the β-amic acid and KOH–EtOH, whereby an equilibrium mixture containing 30% of the *neo*-acid is obtained. The *Na* and NH_4 salts, *Me* ester, m. p. 213·5° (prepared by means of diazomethane), and *Et* ester, m. p. 139°, are described. Treatment of the esters with HNO_2 and AcOH affords (b) *Me* neo*truxinate*, m. p. 234° (obtained readily by partial esterification of *neo*truxinic acid with MeOH and HCl), and the (b) *Et* ester, m. p. 123°. The position of the Me group in the (*b*) MeH ester is established as follows. *neo*Truxinic acid is treated successively with $SOCl_2$ and $AlCl_3$, whereby the *keto-acid* (II), m. p. 224° (*oxime*; *Me* ester, m. p. 124°), is obtained. The last-named ester is also obtained when Me H *neo*truxinate, m. p. 234°, is transformed into its chloride and then treated with $AlCl_3$. (The isomeric ester does not afford a truxinone derivative.) The union of the keto-group to the vicinal and not to the diametrically opposite Ph group in the keto-acid follows from the conversion of the latter by dry distillation into *trans*-cinnamic acid and *indone*, b. p. 69—70°/0·35 mm. (*dibromide*, m. p. 64—65°; *semicarbazone*) (prepared by the action of $NaNH_2$ and nitrosodimethylaniline on indene and subsequent hydrolysis with dil. H_2SO_4). Partial hydrolysis of Me_2 and Et_2 *neo*truxinates yields the (*a*) *Me*, m. p. 139°, and (*a*) *Et*, m. p. 163—164°, *H truxinates.* Conversion of the *a* esters into the chlorides and amides and cautious hydrolysis of the latter affords β-truxinamic acid. Treatment of *neo*truxinic acid in C_6H_6 with a deficiency of $SOCl_2$ and then with NH_3 gives a mixture of NH_4 *neo*truxinate, *neo*truxindiamide, m. p. 249°, *neo*truxin-*a*-amic acid, and neo*truxin*-b-*amic acid*, m. p. 213° [*Na* salt; *Me* ester, m. p. 153—154°, prepared also from the (*a*) *Me H* ester by successive action of $SOCl_2$ and NH_3]. a-*Et* neo*truxin*-b-*amic acid* has m. p. 142—143°.



(I.)



(II.)

H. WREN.

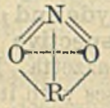
Bile acids. XXXII. M. SCHENCK (Z. physiol. Chem., 1931, **203**, 76—82; cf. A., 1931, 1293).—The nitroso-compound, $C_{24}H_{33}O_8N$, obtained by the action of HNO_3 on *iso*bilianic acid dioxime (A., 1931, 352), with NaOH yields *iso*bilianic acid, and with Zn dust and AcOH, and probably also with H_2SO_4, *iso*bilianic acid 12-monoxime. J. H. BIRKINSHAW.

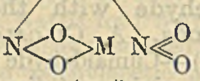
Oxidation of toluene by oxides of nitrogen. A. GIACALONE (Gazzetta, 1931, **61**, 828—832).—A solution of PhMe in AcOH saturated with N oxides in a sealed tube contains after exposure to light for 1 month or heating at 120° PhCHO, BzOH, and small amounts of nitration products. E. E. J. MARLER.

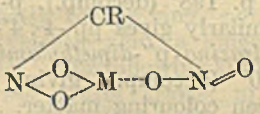
Condensation of aldehydes with hydrazones. VI. Condensation of cumaldehyde and *p*-aminobenzaldehyde with their respective phenylhydrazones. A. GIACALONE (Gazzetta, 1931, **61**, 826—828).—Cumaldehyde condenses with its phenylhydrazone giving pp′-*dicumylidenedihydrazino*-p″-iso-*propyltriphenylmethane*, m. p. 198° (decomp.). p-*Dimethylaminobenzaldehyde* similarly gives pp′-4 : 4′-*dimethylaminobenzylidenedihydrazino*-p″-*dimethylaminotriphenylmethane*, m. p. 220° (decomp.), giving on oxidation with PbO_2 a green colouring matter.

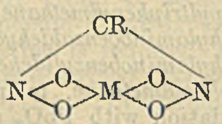
E. E. J. MARLER.

Optical and chemical changes of organic nitro-derivatives and the stereochemical explanation of their isomerisms. A. HANTZSCH (Annalen, 1931, **492**, 65—104).—The variations in colour of NO_2-compounds (existing in one form only in the solid state, *e.g.*, nitroquinol Me_2 ether, for which absorption spectra curves in H_2O, $CHCl_3$, and light petroleum are given) in various solvents is due to the formation of additive compounds of the type $R·NO_2$–solvent (the phenomenon is termed solvatochromism) and absorption is stronger the more unsaturated is the solvent. The differences in the absorption spectra of 3-nitro-*p*-acet-toluidide [existing in two chromoisomeric forms (cf. A., 1909, i, 331)] in EtOH–$CHCl_3$, EtOH, and H_2O are due to isomerisation of each form (in solution) to the same equilibrium, the position of which depends on a sp. action of the solvent. Solvatochromism is often an indication of chromoisomerism. The various types of heteropolar and homopolar chromoisomeric NO_2-compounds are reviewed. The structures for the metallic derivatives of *p*-$NO_2·C_6H_4·CH_2·CO_2Et$ suggested by Lifschitz (A., 1916, i, 45) are excluded, since the metal in all *aci*-NO_2-salts is ionogenically attached to both O atoms of the NO_2-group. The following is a brief summary of the conclusions regarding the structures of chromoisomeric salts. Colourless, yellow, and red salts of $CHR(NO_2)_2$ [R=H, Ph, anisyl] are represented as $NO_2\cdot CR:NO_2\cdot M$, $\left.CR<\begin{smallmatrix}NO_2\\ONO\end{smallmatrix}\right\}M$, and $\left.CR<\begin{smallmatrix}NO_2\\NO_2\end{smallmatrix}\right\}M$, respectively. The corresponding salts of the nitrobenzaldoximes are assigned the constitutions $NO_2\cdot C_6H_4\cdot CH:NO\cdot M$, $\underset{O\cdots M\cdots O}{ON\cdot C_6H_4\cdot CH:N}$, and $\underset{O_2\cdots M\cdots O}{N\cdot C_6H_4\cdot CH:N}$, respectively; analogous formulæ are given for the salts of p-$NO_2\cdot C_6H_4\cdot N:N\cdot OH$, nitroenols ($NO_2\cdot CR:CR'\cdot OH$), and nitrophenols. The structures assigned to the colourless (probably exist only in solution) and coloured forms of $NO_2\cdot C_6H_4\cdot NR_2$ and related compounds are discussed on the basis of the structures $Ar<\begin{smallmatrix}NR_2\\O_2N\end{smallmatrix}$ (colourless), $\left.Ar<\begin{smallmatrix}NR_2\\ONO\end{smallmatrix}\right)$ (yellow), and $\left.Ar<\begin{smallmatrix}NR_2\\NO_2\end{smallmatrix}\right)$ (red). The existence of homochromoisomerides (cf. A., 1910, i, 474) can be explained by assuming that a nitro-compound ($R\cdot NO_2$) possesses a (not regular) tetrahedral configuration (as *A*). On this basis, the colourless, yellow, and red salts of $CHR(NO_2)_2$ (cf. above) are assigned the following *anti*-, *amphi*-, and *syn*-structures, respectively, which are plane-projection formulæ.


(*A*)


(*anti*)


(*amphi*)


(*syn*)

Attention is directed to various examples (lit.) of homochromoisomerism, and the cases of 2 : 4-dinitro-2′-methyldiphenylamine (*loc. cit.*) and *pp′p″*-trinitrotriphenylcarbinol (see below) are discussed.

[With F. Hein.] *pp′p″*-Trinitrotriphenylcarbinol exists in 3 (and possibly 4) unimol. homochromoisomeric forms, having identical absorption spectra in MeOH or $CHCl_3$. When dry CO_2-free air is passed through a solution of *pp′p″*-trinitrotriphenylmethane and EtOH–NaOEt (1+mol.) in C_6H_6 at 0°, the reaction mixture diluted with Et_2O, decomposed with H_2O, evaporated in vac., and the resultant product crystallised from MeOH at room temp., the form of m. p. 167° (*syn–syn–syn*) is obtained. This isomerises only slowly both in the solid state and in solution. Crystallisation of this has given forms of m. p. 175° (*syn–syn–anti*) and 180—182° (*syn–anti–anti*) (obtained in one case only and in very small amount). The stable (*anti–anti–anti*) form has m. p. 189°. The Tl_2 salt of *s*-tetranitroethane has been obtained in yellow and red (unstable) forms.

[With Kanasirski.] The following salts are prepared; the anhyd. forms are usually obtained from the hydrated salts at 130—150°: *anti-p*-nitrobenzaldoxime [*NH_4*, colourless; *Na*, yellow (+$2H_2O$), green (+$2H_2O$), and pale yellow (anhyd.); *K*, red (+$0{\cdot}25H_2O$), red (+EtOH), yellow (+$3H_2O$); *Rb*, yellow (+$2H_2O$) and red (anhyd.); *Cs*, orange (+0·5EtOH), yellow (hydrated), red (anhyd.), passing at 150° into a violet form; *Tl*, red (anhyd.) and yellow (composition $C_7H_6O_3N_2,C_7H_5O_3N_2Tl$); *Ag*, yellow]; *syn-p*-nitrobenzaldoxime (*NH_4*, colourless; *Na*, yellow (+$3H_2O$) and brownish-green (anhyd.); *K*, yellow (+H_2O), green (+H_2O) (formed from the anhyd. red salt in moist air); *Rb*, yellow (hydrated) and red (anhyd.); *Cs*, yellow (hydrated) and red (anhyd.); *Tl*, red (anhyd.); *Ag*, yellow]; *anti-o*-nitrobenzaldoxime [*NH_4*, colourless; *Na*, yellow (+$4H_2O$), red (anhyd.); *K*, yellow (+$4H_2O$), red (anhyd.); *Rb* and *Cs*, yellow (hydrated), red (anhyd.); *Tl*, red]; *anti-m*-nitrobenzaldoxime [*NH_4*, colourless; *Na*, *K*, *Rb*, and *Cs* in yellow (hydrated) and red (anhyd.) forms; *Tl*, red; *Ag*, yellow]. Unstable red and yellow Na salts of *anti-p*-nitrobenzaldoxime are described also. Yellow (+$2H_2O$) and red (anhyd.) *K*, yellow (+$2H_2O$) and almost colourless (anhyd.) *Na*, and colourless (anhyd.) *Ag* (*compounds* with NH_3 and pyridine) salts of p-$NO_2\cdot C_6H_4\cdot N:N\cdot OH$ are prepared. A very unstable yellow compound is obtained from colourless trinitroanisole and hexane.

[With E. Leskien.] 3-Nitro-4-hydroxybenzoic acid [*Na_2* (+H_2O), *K_2* (+$4H_2O$), *Rb_2* (+$4H_2O$), *Cs_2* (+$3H_2O$), all varying shades of red; *Li_2*, reddish-yellow (+$4{\cdot}5H_2O$) and red (+$5H_2O$), both giving golden-yellow (+$2H_2O$) and brick-red (anhyd.) forms, salts described] is isolated in colourless (from H_2O, EtOH, $CHCl_3$, C_6H_6) and yellow (from Et_2O) forms; the latter passes into the former at 70—80°. The Me ester separates from a conc. EtOH solution in colourless needles which pass slowly into the stable yellow form. *m*- and p-$NO_2\cdot C_6H_4\cdot OH$ with EtOH–NaOEt or –KOEt at −7° give colourless salts which change rapidly (below 0°) into coloured forms; picric acid behaves similarly. Pentamethylenediamine and solid picric acid afford a red salt which isomerises slowly to a yellow form. The absorption spectrum of *o*-nitroaniline varies considerably in H_2O, MeOH, and light petroleum, probably owing to the formation of the yellow (unknown) chromoisomeride in solution. 3-Nitro-*p*-toluidine shows the same spectrum in these solvents as does *p*-nitroacetanilide in MeOH and $CHCl_3$; in these cases the second chromoisomeride is apparently incapable of existence, probably because of steric hindrance.

H. Burton.

Atomic grouping in salicylaldoxime, specific for copper. F. Feigl and A. Bondi (Ber., 1931, 64, [*B*], 2819—2823; cf. A., 1930, 1394; 1931, 813).—The *compound* $C_6H_4<\begin{smallmatrix}CH{=}NO\\O{-\!-}Cu\end{smallmatrix}$ is obtained from Fehling's solution and salicylaldoxime or by digestion of Ephraim's salt (*loc. cit.*) with Na_2CO_3 or NaOH and aq. EtOH. It is converted by AcOH into the salt $C_6H_4<\begin{smallmatrix}CH:N\cdot OH\\O{-}Cu/_2\end{smallmatrix}$, the constitution of which is supported by the ability of *salicylaldoxime Me ether*, b. p. 107°/14 mm., m. p. 28° (from salicylaldehyde and *O*-methylhydroxylamine hydrochloride), to give a *Cu* compound $(C_8H_8O_2N)_2Cu$, whereas *o*-methoxybenzaldoxime does not react. Ph γγγ-trichloro-β-hydroxy-*n*-propyl ketoxime and *Me* β-*hydroxy*-n-*propyl ketoxime*, b. p. 123—124°/13 mm., do not-yield Cu compounds, although they contain the Cu-sp. grouping $\mathrm{OH\cdot\underset{\cdot}{\dot{C}}\cdot\underset{\cdot}{\dot{C}}\cdot\underset{\cdot}{C}\colon N\cdot OH}$. H. WREN.

Synthesis of *p*-alkoxymethylbenzaldehydes. S. SABETAY (Compt. rend., 1931, **193**, 1194—1195).—Interaction of ωωω′-tribromo-*p*-xylene (isolated from the products of bromination of *p*-xylene at 140—150°) with NaOEt and EtOH gives p-*ethoxymethylbenzaldehyde diethylacetal*, b. p. 142°/14 mm., which is hydrolysed by aq. H_2SO_4–AcOH to p-*ethoxymethylbenzaldehyde*, b. p. 133—134°/14 mm. (*phenylhydrazone*, m. p. 86°). *p*-Methoxymethylbenzaldehyde (this vol., 57) and its *dimethylacetal*, b. p. 122—123°/16 mm., are similarly prepared. H. A. PIGGOTT.

Lignin and related compounds. LXI. Ethers of glycol-lignin. H. HIBBERT and L. MARION (Canad. J. Res., 1931, **5**, 302—305; cf. A., 1931, 828).—Glycol-lignin and NaOEt in EtOH give a *Na* salt, converted by chloro-2 : 4-dinitrobenzene in PhMe into a *dinitrophenyl ether*, and by chlorodimethyl ether into a *methoxymethyl ether*. The dinitrophenyl ether gives a *Me ether* under mild conditions of methylation, whilst a higher temp. and excess of NaOH removes the dinitrophenyl group, the resulting *Me ether* having a lower OMe content than fully methylated glycol-lignin. A. A. LEVI.

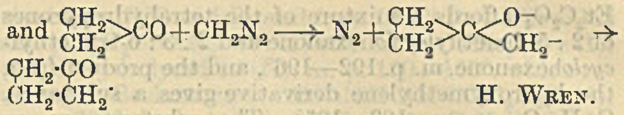
Lignin of pinewood. B. RASSOW and H. GABRIEL (Cellulosechem., 1931, **12**, 318—320; cf. A., 1931, 1401).—Glycol-lignin (mol. wt. in phenol 569) is amorphous and has colloidal properties. It is converted by hot H_2O, cold conc. HCl, or drying above 90° into a dark insol. substance. The residue obtained after extraction of the wood with glycol and HCl contains 43—50% of cellulose, and is purer and contains less pentosan than other wood celluloses. R. S. CAHN.

Preparation of syringic aldehyde [4-hydroxy-3 : 5-dimethoxybenzaldehyde]. W. M. MCCORD (J. Amer. Chem. Soc., 1931, **53**, 4181—4183).—Gallic acid Me_3 ether and H_2SO_4 give syringic acid [*amide* (I), m. p. 192°; *anilide* (II), m. p. 146°, of Ac derivative]. (I) and PCl_5 in PhMe afford the *iminochloride hydrochloride*, m. p. 145°, converted by warm pyridine into the *Ac* derivative (III), m. p. 142°, of *syringonitrile*, m. p. 129°; (III) is converted by Stephen's method into syringaldehyde. (II) and PCl_5 in PhMe give the corresponding *phenyliminochloride*, m. p. 136°. C. J. WEST (*b*).

Preparation of trimethylgallaldehyde. M. NIERENSTEIN (J. pr. Chem., 1931, [ii], **132**, 200).—Details are given for the prep. of trimethylgallaldehyde in 75·5% yield by hydrogenation of galloyl chloride Me_3 ether. R. S. CAHN.

New route to *cyclo*butanone. P. LIPP and R. KÖSTER (Ber., 1931, **64**, [*B*], 2823—2825).—Passage of keten into diazomethane in anhyd. Et_2O yields *cyclo*butanone [semicarbazone, 211—212° (corr.) when slowly heated], probably according to the scheme:

$$\mathrm{CH_2\colon CO+CH_2N_2\longrightarrow \begin{array}{l}CH_2\cdot CO\\ CH_2-N\end{array}\!\!\gg N\longrightarrow N_2+\begin{array}{l}CH_2\\ CH_2\end{array}\!\!>CO}$$



$$\text{and }\mathrm{\begin{array}{l}CH_2\\ CH_2\end{array}\!\!>CO+CH_2N_2\longrightarrow N_2+\begin{array}{l}CH_2\\ CH_2\end{array}\!\!>C\!<\!\begin{array}{l}O-\\ CH_2-\end{array}\rightarrow \begin{array}{l}CH_2\cdot CO\\ CH_2\cdot CH_2\end{array}}.$$

H. WREN.

Orientation phenomena among the *cyclo*hexanones. VI. Methylation of inactive 2-methyl*cyclo*hexanone. VII. Allylation of inactive 2-methyl*cyclo*hexanone and methylation of 1-menthone. R. CORNUBERT and R. HUMEAU. **VIII. Allylation and benzylation of *cyclo*hexanone. Alkylation of *cyclo*hexanones with sodamide. IX. Methylation of 2 : 3-dimethyl*cyclo*hexanone. X. Methylation of 2 : 4-dimethyl*cyclo*hexanone.** R. CORNUBERT and A. MAUREL (Bull. Soc. chim., 1931, [iv], **49**, 1468—1487, 1487—1497, 1498—1515, 1515—1523, 1523—1528; cf. A., 1931, 1417).—VI. Methylation of 2-methyl*cyclo*hexanone with $NaNH_2$ and Me_2SO_4 in Et_2O affords a fraction, b. p. 172—176°, containing a mixture of 2 : 5-dimethyl*cyclo*hexanone (oxime, m. p. 108—109°) and pulenone (2 : 2 : 5-trimethyl*cyclo*hexanone) characterised as oximes, together with a fraction, b. p. 187—191°, d^{15} 0·9097, probably containing 2 : 5 : 6-trimethyl*cyclo*hexanone (liquid oxime). The intermediate fraction, b. p. 180—190°, after extraction with $NaHSO_3$ with PhCHO in presence of HCl affords (1) a fraction b. p. 180—210°/14 mm., containing *benzylidenepulenone*, m. p. 89—90°, and *substances* of m. p. 109—109·5° and m. p. 73°, and (2) fractions b. p. 210—240°/14 mm. and 240—262°/14 mm., containing the *tetrahydropyrones*, m. p. 133—137° and 190—195°, of 2 : 5-dimethyl- and 2 : 5 : 6-trimethyl-*cyclo*hexanone. The original fraction, b. p. 187—191°, with PhCHO in presence of HCl similarly affords benzylidenepulenone and the tetrahydropyrone of 2 : 3 : 6-trimethyl*cyclo*hexanone. The monomethylation products, b. p. 178—185°, with PhCHO and HCl similarly yield a fraction, b. p. 150—215°/20 mm., containing benzylidene compounds, affording a semicarbazone, m. p. 220—221°, possibly a mixture of the semicarbazones of benzylidene-2 : 5-dimethyl- and -2 : 2 : 5-trimethyl-*cyclo*hexanone, and fractions, b. p. 215—245°/20 mm., 245—270°/20 mm., containing the tetrahydropyrones of -2 : 5-di- and 2 : 2 : 5-tri-methyl*cyclo*hexanones. The yield of 2 : 5-dimethyl*cyclo*hexanone amounts to about 55%. Obtained by condensation of 2-methyl*cyclo*hexanone with $Et_2C_2O_4$ in presence of NaOEt, alkylation with MeI and elimination of $H_2C_2O_4$, and separation with HCl, 2 : 5-dimethyl*cyclo*hexanone has b. p. 76—77°/27 mm., d^{15} 0·906 (semicarbazone, m. p. 168—168·5°), and gives a mixture of tetrahydropyrones, m. p. 103—107° and 133—137°. Pulenone, b. p. 182—184°, d^{24} 0·8871 (oxime, m. p. 94°; semicarbazone, m. p. 169—170°), with PhCHO in presence of HCl at −15° yields benzylidenepulenone, m. p. 90° (*hydrochloride*, m. p. 106°; *semicarbazone*, m. p. 158·5—159°). 2 : 3 : 6-Trimethyl*cyclo*hexanone, b. p. 79—80°/20 mm., d^{21} 0·9058, obtained in low yield by condensation of $Et_2C_2O_4$ and 2 : 5-dimethyl*cyclo*hexanone, is better prepared from 2 : 5-dimethyl*cyclo*hexanone and amyl formate in presence of $NaNH_2$ and hydrogenation of the hydroxymethylene derivative in presence of Pd. The product from

$Et_2C_2O_4$ affords a mixture of the tetrahydropyrones of 2 : 5-dimethyl*cyclo*hexanone and 2 : 3 : 6-trimethyl*cyclo*hexanone, m. p. 192—196°, and the product from the hydroxymethylene derivative gives a substance, $C_{23}H_{26}O_2$, m. p. 183—185°. The substance, m. p. 73°, obtained from the methylation product is not 5-hydroxybenzyl-2-methyl*cyclo*hexanone, the latter, obtained, together with a little 5 : 5-dihydroxybenzyl-2-methyl*cyclo*hexanone, by Vorländer and Kunze's method, having m. p. 106·5—107°. The *benzylidene* derivative of 2-methyl*cyclo*hexanone has m. p. 42—43°, the dibenzylidene derivative, m. p. 118—118·5°. Methylation of 2 : 5-dimethyl*cyclo*hexanone with $NaNH_2$ and Me_2SO_4 in Et_2O affords only pulenone. In the disodiation of 3-methyl*cyclo*hexanone, 2 : 3 : 6-trimethyl*cyclo*hexanone is formed as well as pulenone and 2 : 5-dimethyl*cyclo*hexanone.

VII. The 3-methyl-6 : 6-diallyl*cyclo*hexanone obtained on allylation of 3-methy*cyclo*hexanone with H_2 in presence of Ni formate at 60—70° affords 3-*methyl*-6 : 6-*dipropyl*cyclo*hexanone*, b. p. 130—131°/23 mm., d^{16} 0·8970 (*benzylidene* derivative, m. p. 83·5—84°). 3-*Methyl*-2 : 6-*diallyl*cyclo*hexanone*, b. p. 118—125°/12 mm., obtained by allylating in a dry tube at 140° for 12 hr. the product obtained by condensation of 3-methyl-2-propyl*cyclo*hexanone and ethyl oxalate in presence of NaOMe, when hydrogenated in presence of Ni formate affords 3-methyl-2 : 6-dipropyl*cyclo*hexanone, yielding a tetrahydropyrone compound, m. p. 156—157°. 5-Methyl-2-propyl*cyclo*hexanone with PhCHO in presence of HCl yields a fraction, b. p. 204—206°/18 mm., and crystals, m. p. 124—126°, but no benzylidene derivative; with 2 mols. of PhCHO fractions b. p. 185—245°/12 mm. and 245—270°/12 mm. were obtained, the latter yielding two tetrahydropyrone compounds, m. p. 88—90° and 127—128°. 2 : 3-*Dimethyl*-6-iso*propyl*cyclo*hexanone*, b. p. 95—97°/12·5 mm., d^{15} 0·905, obtained by hydrogenation in presence of Pd of hydroxymethylenementhone, b. p. 124—125°/16 mm. (yield 50% from menthone), yields a *tetrahydropyrone*, m. p. 99—100°. The chloromenthone, b. p. 113—120°/16 mm., obtained by chlorination of menthone in presence of $CaCO_3$, with MgMeI yields a methylmenthone, b. p. 104—110°/21 mm., which still contains 2·7% Cl; a dichloromenthone, m. p. 64·5—65°, is simultaneously obtained. Methylation of menthone by the $NaNH_2$ process yields a methylmenthone, b. p. 100°/17 mm., $d^{13·5}$ 0·9124 (semicarbazone, m. p. 193—195°), yielding a benzylidene derivative, b. p. 192—194°/16 mm., probably a mixture of isomerides. The benzylidene derivative obtained directly from the methylation product contains a small amount of substance, b. p. 185—195°/12 mm. and 225—260°, from which, however, no tetrahydropyrone was deposited.

VIII. In the allylation of *cyclo*hexanone with allyl bromide, the yield of allyl*cyclo*hexanone, b. p. 97—98°/20 mm., is increased from 20% to 50% by using double the vol. of Et_2O, the yield of diallyl*cyclo*hexanone increasing simultaneously. Allylation of allyl*cyclo*hexanone affords a mixture, b. p. 114—123°/16 mm., of diallyl*cyclo*hexanones, hydrogenated to about 87% of 2 : 2-dipropyl*cyclo*hexanone, b. p. 123—126°/20 mm. (*benzylidene* derivative, m. p. 48°), and 13% of 2 : 6-dipropyl*cyclo*hexanone (*tetrahydropyrone*, m. p. 127—127·5°). The direct diallylation of *cyclo*hexanone yields a mixture of diallyl*cyclo*hexanones, b. p. 114—123°/14 mm., converted on hydrogenation into a mixture of dipropyl*cyclo*hexanones, b. p. 120—123°/20 mm., containing 91% of 2 : 2- and 9% of 2 : 6-derivative. In presence of the Na derivative of *cyclo*hexanone, allyl*cyclo*hexanone and allyl bromide gave three times the normal yield of diallyl*cyclo*hexanone, in which the 2 : 2-isomeride predominated, but the difference is possibly due in part to differences in concn. Benzyl*cyclo*hexanone under similar conditions with the Na derivative of allyl*cyclo*hexanone yields a benzylallyl*cyclo*hexanone, b. p. 178—190°/16 mm., hydrogenated to 2-benzyl-2-propyl*cyclo*hexanone, b. p. 176—179°/13 mm. (*semicarbazone*, m. p. 203°; *benzylidene* derivative, b. p. 257—260°/14 mm.). 2 : 6-Dipropyl*cyclo*hexanone, b. p. 115—115·5°, d^{14} 0·8955 (tetrahydropyrone, m. p. 128°), is also obtained by hydrogenation of 2-*allyl*-6-*propyl*cyclo*hexanone*, b. p. 108—109°/12 mm., d^{15} 0·9122, prepared from 2-propyl*cyclo*hexanone, ethyl oxalate, and NaOMe at −15°, followed by allylation with allyl bromide at 145—150° for 9 hr. 2′ : 2-Dipropyl*cyclo*hexanone, b. p. 120—121°/18 mm., $d^{15·5}$ 0·9086, is obtained in 19% yield by regeneration from the benzylidene derivative. Hydrogenation of 2 : 2-diallyl*cyclo*hexanone in presence of Ni formate is very sensitive to temp. and does not occur at 60—68° Above 70° it is very rapid and the range 68—70° must be strictly maintained. Use of MeOH, $Bu^{\beta}OH$, or *iso*amyl alcohol in place of EtOH in regenerating the ketone from the benzylidene derivative is less effective, amyl alcohol affording a liquid, b. p. 105—112°/22 mm. Similarly with amyl-alcoholic KOH the benzylidene derivative of 2-methyl*cyclo*hexanone affords a liquid, $C_{17}H_{30}O_2$, b. p. 107—109°/20 mm., d^{11} 0·9201, representing a condensation of 1 mol. of 2-methyl*cyclo*hexanone and 2 mols. of *iso*valeraldehyde. Allyl bromide was obtained in only 37% yield by Merlin and Jacobi's method. By passing HBr into allyl alcohol below 0° until about 5% more than the theoretical increase in wt. occurs and leaving 12—15 hr. a yield of 80—85% is obtained. Benzylation of *cyclo*hexanone in Et_2O with $NaNH_2$ and CH_2PhBr affords 2-benzyl*cyclo*hexanone, b. p. 167—168°/20 mm., m.p. 30°, d^{23} 1·0298 (*semicarbazone*, m. p. 170—171°; *benzylidene* derivative, m. p. 75—76°, b. p. 267°/25 mm.), together with a fraction, b. p. 224—225°/13 mm., containing benzyl*cyclo*hexylidene*cyclo*hexanone (*oxime*, m. p. 198—199°), and a residue, containing 2 : 2-dibenzyl*cyclo*hexanone, m. p. 53—54° (*oxime*, m. p. 121°; *benzylidene* derivative, m. p. 105—106°, yielding tribenzyl*cyclo*hexanone, m. p. 57—58°, on hydrogenation), also obtained together with 2 : 6-dibenzyl*cyclo*hexanone, m. p. 103°, by benzylation of 2-benzyl*cyclo*hexanone.

IX. 2 : 3-Dimethyl*cyclo*hexanone, b. p. 78°/24 mm., d^{20} 0·9159 (semicarbazone, b. p. 202—203°), has been obtained as follows: Et acetoacetate is condensed with trioxymethylene in presence of piperidine, the reduction product of Et 3-methyl*cyclo*hexan-3-ol-1-one-4 : 6-dicarboxylate, m. p. 90—92°, converted into Et 3-methyl-Δ^2-*cyclo*hexenone-4-carboxylate (yield

20%), b. p. 135—136°/9 mm., d^{20} 1·0702, which on successive methylation, hydrolysis, and hydrogenation gives Et 2 : 3-*dimethyl*-Δ^2-cyclo*hexenone-4-carboxylate,* b. p. 138—139°/10 mm., d^{20} 1·0659, 2 : 3-dimethyl-Δ^2-*cyclo*hexenone, b. p. 86°/13 mm., d^{15} 0·9725 (semicarbazone, m. p. 218—220°), and 2 : 3-dimethyl*cyclo*hexanone. Methylation of the last with MeI and $NaNH_2$ in Et_2O affords 67% of 2 : 2 : 3-trimethyl*cyclo*hexanone (*benzylidene* derivative, m. p. 85—86°) and 33% of 2 : 3 : 6-trimethyl*cyclo*hexanone (*tetrahydropyrone* compounds, m. p. 168—169° and 190—192°) calc. from the wts. of crude benzylidene and tetrahydropyrone formed or 77% and 23%, respectively, calc. on the cryst. products.

X. 2 : 4-Dimethyl*cyclo*hexanone, b. p. 70—71°/16 mm., $d^{15\cdot5}$ 0·91 (oxime, m. p. 98—99°), obtained from 4-methyl*cyclo*hexanone, $NaNH_2$, and Me_2SO_4 in Et_2O, from $Et_2C_2O_4$ and 4-methyl*cyclo*hexanone in presence of NaOMe or NaOEt, and heating with MeI, or from the hydroxymethylene derivative of 4-methyl*cyclo*hexanone, b. p. 106—109°/27 mm., by hydrogenation in presence of Pd, similarly affords a mixture, b. p. 74—76°/16 mm., of about 95% of 2 : 2 : 4-*trimethyl*cyclo*hexanone* (*benzylidene* derivative, m. p. 91—92°) and about 5% of 2 : 4 : 6-*trimethyl*cyclo*hexanone,* b. p. 85—87°/23 mm., d^{19} 0·902 (*semicarbazone,* m. p. 222°; *tetrahydropyrone,* m. p. 203°), also obtained by hydrogenation in presence of Pd of the hydroxymethylene derivative, b. p. 102·5—104°/17 mm., prepared from 2 : 4-dimethyl*cyclo*hexanone, $NaNH_2$, and amyl formate.

R. BRIGHTMAN.

Preparation of ketochloroimines. C. R. HAUSER, G. J. HAUS, and H. HUMBLE (J. Amer. Chem. Soc., 1931, **53**, 4225—4226).—$CPh_2{:}N\cdot MgBr$ and an equiv. of Cl_2 in the cold give a product containing about 60% of benzophenonechloroimine. The Mg compound from p-$C_6H_4Cl\cdot CN$ similarly affords a chloroimine, m. p. 103—104°; a bromoimine can be prepared. Details are to be published later. C. J. WEST (*b*).

Oximes of αβ-unsaturated ketones and the Beckmann rearrangement. II. A. H. BLATT and J. F. STONE, jun. (J. Amer. Chem. Soc., 1931, **53**, 4134—4149; cf. A., 1931, 621).—The previously described oxime of p-$C_6H_4Br\cdot CO\cdot CH{:}CHPh$ is a mixture of the *syn* (I) and *anti* (II) isomerides, since hydrolysis of its Beckmann rearrangement product gives NH_3 and p-$C_6H_4Br\cdot CO_2H$. Separation of (I) and (II) by fractional crystallisation was unsuccessful, but acetylation and fractional crystallisation from AcOEt gives the syn-*acetate* (III), m. p. 145°, and the anti-*acetate* (IV), possibly not entirely free from (III), m. p. 105—106°. (III) gives a *Br_2*-derivative (V), m. p. 146—147°, also obtained by acetylating (VII). (V) and KI in $COMe_2$ give (III). Hydrolysis of (III) with EtOH–KOH gives 80% of (I), m. p. 145—158° according to rate of heating, partly converted into (II) by prolonged boiling with EtOH–KOH, heating with HCO_2H, and reaction with MgEtBr. The Beckmann rearrangement of (I) gives cinnam-p-bromoanilide (VI), whilst the Br_2-derivative (VII), m. p. 173°, from (III) and Br affords *αβ-dibromo-β-phenylpropion*-p-*bromoanilide,* m. p. 195—196°; also synthesised from (VI) and Br and from $CHPhBr\cdot CHBr\cdot COCl$ and p-$C_6H_4Br\cdot NH_2$. (VII) and KI in $COMe_2$ give (I). (IV) is hydrolysed to (II), m. p. 150—163°, which rearranges (Beckmann) to $CHPh{:}CH\cdot NH\cdot CO\cdot C_6H_4Br$(?), m. p. 204°, hydrolysed to NH_3 and p-$C_6H_4Br\cdot CO_2H$. (II) and Br give (VII); it is not possible to say whether this shift in configuration is due to the saturation of the double linking or to a sp. isomerising action of the reagent. Since it has been suggested by von Auwers that thermal decomp. of (VII) to the *iso*oxazole (cf. *loc. cit.*) might proceed through the *α-bromo-oxime* (VIII), $CHPh{:}CBr\cdot C({:}NOH)\cdot C_6H_4Br$, m. p. 163—164°, this was prepared from the reaction product of the Br_2-ketone and EtOH–KOAc (without isolating the α-Br-ketone) and NH_2OH,HCl. Hydrolysis of the Beckmann rearrangement product of (VIII) gives NH_3 and p-$C_6H_4Br\cdot CO_2H$, but when (VIII) is heated the *iso*oxazole is not produced; (VIII), therefore, probably has the *anti*-configuration. (VIII) is unaffected by dissolution in conc. H_2SO_4, as is the oxime of α-bromobenzylideneacetophenone. *Benzylidenedeoxybenzoinoxime,* m. p. 208° (cf. Knoevenagel and Weissgerber, A., 1893, i, 353), undergoes the Beckmann rearrangement, forming BzOH and deoxybenzoin, whilst treatment with H_2SO_4 gives a red oil, from which neither of the two known forms of 3 : 4 : 5-triphenyl*iso*oxazoline could be isolated. The oxime, m. p. 149—153°, of Ph β-phenylstyryl ketone undergoes the Beckmann rearrangement, yielding β-*phenylcinnamanilide,* m. p. 130—131°, whilst treatment with H_2SO_4 gives 3 : 4 : 5-triphenyl*iso*oxazoline, m. p. 139°. The formation of *iso*oxazolines from αβ-unsaturated ketones does not proceed through an oxime as an intermediary but through a complex bimol. 1 : 4-additive process. The work of von Auwers and Seyfried (A., 1931, 223) is discussed; the divergent conclusions reached by these authors are due to the different emphasis and interpretation placed on the reaction of the bromo-oximes and alkali. C. J. WEST (*b*).

Reduction product of benzylidenepinacolone (styryl *tert.*-butyl ketone). G. A. HILL and S. SUSSELMAN (J. Amer. Chem. Soc., 1931, **53**, 4424—4428).—The compound, m. p. 142°, previously thought (A., 1923, i, 789) to be β-phenylethyl*tert.*-butylcarbinol (cf. A., 1930, 343) is probably a *stereoisomeride* (I) (m. p. 147°) of εζ-diphenyl-ββιι-tetramethyldecan-γθ-dione, m. p. 208° (cf. *loc. cit.*). The homogeneity of (I) is shown by crystallisation experiments, cooling curves, analysis, and mol. wt.; its structure is established by the action of MgMeI. C. J. WEST (*b*).

Nitration in the fluorene series. E. LANGECKER (J. pr. Chem., 1931, [ii], **132**, 145—152).—Attempts to prepare 1- or 1 : 8-substituted fluorenone derivatives were unsuccessful. 9-Acetamidofluorene (modified prep. from fluorenoneoxime) gives, when nitrated by Kuhn's method (A., 1925, i, 1260), 2-nitrofluorenone and other products, whilst with conc. HNO_3 in Ac_2O 2 : 7-dinitrofluorenone is formed together with an *isomeride,* m. p. 236—237°, giving a *diamino*-compound, m. p. 196° (*Ac_2* derivative, m. p. above 290°). Fluorenoneoxime and conc. HNO_3 in Ac_2O give an unstable substance, probably of the 9-oximinofluorene type, which with H_2SO_4 in boiling AcOH gives a *dinitrofluorenone*, m. p. above 300° (reduced to a *nitroaminofluorenone*, m. p. 243—244°, by Na_2S), and 2-nitrofluorenone; cold, fuming HNO_3 gives a similar unstable substance, which forms 2 : 7-dinitrofluorenone on oxidation. *O*-Acetylfluorenoneoxime and conc. HNO_3 in Ac_2O at 30—40° give the 2-*nitro*-compound, m. p. 228°, hydrolysed by KOH or conc. H_2SO_4 to 2-*nitrofluorenoneoxime*, m. p. 249° (decomp.), which was prepared also from 2-nitrofluorenone, which it yields on oxidation by $Na_2Cr_2O_7$ in AcOH.

R. S. Cahn.

Haloform reaction. IV. Influence of *o*-methoxy-groups. R. C. Fuson, M. W. Farlow, and C. J. Stehman (J. Amer. Chem. Soc., 1931, **53**, 4097—4103).—In no case has it been found possible to isolate the trihalogenomethyl intermediate using acetophenones with only one *o*-substituent. 2 : 4 : 6-Trimethoxyacetophenone and NaOBr in dil. or conc. alkali give ααα-*tribromo*-2 : 4 : 6-*trimethoxyacetophenone*, m. p. 102·5—103° (corr.), in 67% and 58% yields, respectively; reaction is about 6 times as fast in dil. alkali. The Cl_3-derivative, m. p. 119—120° (corr.), results in 68% yield. Both halogeno-compounds are oxidised to 2 : 4 : 6-trimethoxybenzoic acid by alkali. 2-Methoxyacetonaphthone and NaOBr in H_2O or in 20% EtOH give 51 or 64% of 2-*methoxy*-1-*tribromoacetylnaphthalene*, m. p. 136·5—137° (corr.) (the 1-*trichloroacetyl* derivative has m. p. 131—131·5°), converted by alkali into 2-methoxy-α-naphthoic acid. The retardation of the haloform reaction is of the same order of magnitude in both cases. Since the effect observed with 2 : 1-OMe·$C_{10}H_6Ac$ is to be ascribed to the combined influences of the OMe and the benzo-groups, it is evident that the separate effect of the benzo-group is similar to that of the OMe group.

C. J. West (*b*).

Action of Grignard solutions on 10-methoxyanthrones. E. de B. Barnett (J.C.S., 1931, 3340—3341).—10-Methoxyanthrone (prep. improved) interacts with $CH_2Ph·MgCl$ in the cold to form anthraquinone, 10 : 10′-dimethoxy-10 : 10′-dianthrone, and 10-*methoxy*-9-*benzyl*-9 : 10-*dihydroanthranol*, m. p. 129°, which with HCl and AcOH gives 10-chloro-9-benzylanthracene. 10-Methoxy-1 : 4-dimethylanthrone with MgMeI (3 mols.) gives 10-*methoxy*-1 : 4 : 9-*trimethyl*-9 : 10-*dihydroanthranol*, m. p. 148°, but this did not give a definite product with HCl–AcOH. A poor yield of 10-phenyl-1 : 4-dimethylanthrone was obtained with PhMgBr, and $CH_2Ph·MgCl$ and Mg *o*-tolyl bromide gave only resinous products.

H. A. Piggott.

Chemical participation of water in the oxidising action of *p*-benzoquinone; theory of oxidative processes. A. Bach and K. Nikolaiev (Ber., 1931, **64**, [*B*], 2769—2772).—In absence of H_2O there is no reaction between *p*-benzoquinone and EtOH when irradiated; reaction increases with increasing amounts of H_2O, although there is no direct proportionality. The presence of H_2O is essential for the oxidation by *p*-benzoquinone of pyrogallol in EtOH, $COMe_2$, or Et_2O or of *p*-phenylenediamine in Et_2O. It is considered that H_2O has a somewhat stabilising effect on the peroxide form of *p*-benzoquinone owing to the formation of *p*-hydroxyphenyl H peroxide, which imparts its active O to the substrate and is therefore deoxidised to quinol. H. Wren.

Complex salts of hydroxyquinones. I. A. Mangani (Gazzetta, 1931, **61**, 820—826).—The *Na* salt of 2-hydroxy-α-naphthaquinone, *Co*, *Mg*, and *Zn* salts of 5-hydroxy-α-naphthaquinone, and *Co* and *Zn* salts of naphthazarin, which are probably additive compounds with Co and Zn acetates, are described. Chrysazin (1 : 8-dihydroxyanthraquinone) forms *hydrogen Co*, *Mg*, *Zn*, and *Cu* salts, the last being a very sensitive test, and a neutral *Co* salt.

E. E. J. Marler.

Hydroxyanthraquinones. I. Synthesis of purpurin. P. G. Marshall (J.C.S., 1931, 3206—3208).—Quinizarin heated with Na_2SO_3 and CuO in H_2O gives an almost quant. yield of the 2-sulphonic acid (I); the Na salt when heated with $Ca(OH)_2$ and H_2O at 250° affords purpurin (84% yield). Zimmermann's method (A., 1930, 941) of prep. of (I) does not give exclusively the 2-sulphonic acid. H. Burton.

Anthrone series. III. Synthesis of 3-methoxyphthalaldehydic acid and a new synthesis of chrysazin. IV. Synthesis of the anthrones derived from chrysophanic acid. C. A. Naylor, jun. [with J. H. Gardner] (J. Amer. Chem. Soc., 1931, **53**, 4109—4113, 4114—4119).—III. Oxidation of 1 : 5-dimethoxynapththalene with alkaline $KMnO_4$ gives 11—16% of 3-*methoxyphthalaldehydic acid* (I), m. p. 121—122° to a turbid liquid, which then partly solidifies and re-melts at 144·8°; all m. p. are corr. *p*-$C_6H_4Br·OH$ and (I) with 85% H_2SO_4 afford 55% of 3-*methoxy*-2-(5-*bromo*-2-*hydroxyphenyl*)*phthalide*, m. p. 198—200°, reduced by Zn and 10% NaOH to 3-*methoxy*-2-o-*hydroxybenzylbenzoic acid*, m. p. 185—186°, which is converted by conc. H_2SO_4 at room temp. into 1-*hydroxy*-8-*methoxy*-10-*anthrone*, m. p. 170—171°. This is oxidised by CrO_3 in AcOH to 1-hydroxy-8-methoxyanthraquinone (chrysazin Me ether), demethylated to chrysazin (11% yield) (Ac_2 derivative, m. p. 231—232°).

IV. 6-Bromo-*m*-cresol and (I) with 85% H_2SO_4 give 3-*methoxy*-2-(5-*bromo*-2-*hydroxy*-4-*methylphenyl*)*phthalide*, m. p. 243—244·6°, convertible (as above) into 3-*methoxy*-2-(2′-*hydroxy*-4′-*methylbenzyl*)*benzoic acid*, m. p. 164—164·6°, and 1-*hydroxy*-8-*methoxy*-3-*methyl*-10-*anthrone* (II), m. p. 173·8—175°. Demethylation of 1-*hydroxy*-8-*methoxy*-3-*methylanthraquinone*, m. p. 202—204°, gives chrysophanic acid (III), identical with the acid prepared by Eder and Widmer's method (A., 1922, i, 260; 1923, i, 688). Reduction of (III) with Sn and conc. HCl in AcOH affords 1 : 8-*dihydroxy*-3-*methyl*-9-*anthrone*, m. p. 203·4—204° (corresponding anthranyl *acetate*, m. p. 236—237°, identical with a product obtained by successive demethylation and acetylation of chrysarobin). Demethylation of (II) gives 1 : 8-*dihydroxy*-3-*methyl*-10-*anthrone*, m. p. 179—180° (corresponding anthranyl *acetate*, m. p. 209—210°), also obtained from 3-*hydroxy*-2-(2′-*hydroxy*-4′-*methylbenzyl*)*benzoic acid*, m. p. 157—158°, which is prepared by reducing the corresponding benzoylbenzoic acid with Zn and aq. NH_3.

C. J. West (*b*).

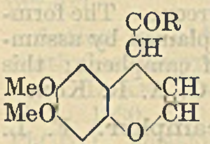
Hydroxy-derivatives of retene. L. F. Fieser and M. N. Young (J. Amer. Chem. Soc., 1931, **53**, 4120—4129).—The C_2 and C_3 atoms of phenanthrene are joined by a single linking and a 2(or 3)-phenanthrol cannot, therefore, couple with diazonium salts if the 1(or 4)-position is substituted, since a double linking is required for the formation of the intermediate additive compound. Using this principle, reduction potential data, and the Dimroth test for α-hydroxyquinones, it is shown that the hydroxyretenes described by Komppa and Wahlforss (A., 1931, 226) are 2-, m. p. 200—202°, and 6-retenols, m. p. 161—162°. Oxidation of 6-acetoxyretene with CrO_3 in AcOH gives 6-*acetoxyretenequinone*, m. p. 200°, hydrolysed by EtOH–KOH to 6-*hydroxyretenequinone* (*Me ether*, m. p. 196°, also prepared by oxidation of 6-*methoxyretene*, m. p. 115—116°). 6-Retenol and $p\text{-}NO_2\cdot C_6H_4\cdot N_2Cl$ in AcOH afford 5-p-*nitrobenzeneazo*-6-*retenol*, decomp. when heated, which could not be reduced smoothly. The Na salt of the dye obtained from diazobenzenesulphonic acid is readily reduced, but the 5-amino-6-retenol could not be obtained pure; the crude amine, Ac_2O, and NaOAc give an *oxazole*, m. p. 112°. Retene-6-sulphonic acid is characterised as the p-*toluidine* salt. 1-*Chlorophenanthraquinone*, m. p. 217—218°, is prepared in poor yield from the 1-sulphonate and $KClO_3$ in HCl; 6-chlororetenequinone could not be obtained by this method. 2-*Acetoxyretene* and 2-*acetoxyretenequinone* have m. p. 160° and 171—172°, respectively. 2-*Hydroxyretenequinone*, m. p. 229—231°, gives a bluish-green coloration with cold, dil. EtOH–alkali changing to reddish-brown when heated. This colour change is reversible and is also shown by phenanthraquinones containing a *m*-OH group to one of the CO groups. Reduction of retenequinone with Zn and AcOH gives 9-*retenol* (I), m. p. 176° (*Me ether*, m. p. 108°; 10-p-*nitrobenzeneazo*-derivative, m. p. 243·5—244·5°), isolated through its *acetate*, m. p. 141°. When a solution of (I) in AcOH is exposed to air for 3 days, a mol. *compound*, m. p. 160—161°, of (I) and retenequinone is obtained. 9-*Acetoxy*-10-*allylretene*, m. p. 102°, is obtained by rearrangement of 9-*allyloxyretene*, m. p. 84°, and subsequent acetylation. Reduction of 1-methylphenanthraquinone [as in the prep. of (I)] gives 1-*methyl*-9-*acetoxyphenanthrene*, m. p. 99—100°, whilst the usual reductive acetylation affords the *quinol diacetate*, m. p. 189°. The potentials of retenequinone and its 2- and 6-OH derivatives are 0·421, 0·385, and 0·348 volts, respectively.

[With H. D. Newman.] The following compounds are described: 2-*allyloxyphenanthrene*, m. p. 92°; 1-*allyl*-2-*phenanthrol*, m. p. 125·5° (*acetate*, m. p. 105°; *coumaran* derivative, m. p. 155°; *allyl ether*, m. p. 91·5°); 4-*allyl*-3-*phenanthrol*, m. p. 91° (*acetate*, m. p. 56°; *coumaran* derivative, m. p. 89°).

C. J. West (*b*).

Manufacture of aminodiazoanthraquinones and of anthraquinone derivatives therefrom. I. G. Farbenind. A.-G.—See B., 1932, 57.

Rotenone. XVI. Interpretation of characteristic reactions of rotenone. F. B. LaForge, H. L. Haller, and L. E. Smith. **XVII. Dimorphic forms of dihydrorotenone.** F. B. LaForge and G. L. Keenan. **XVIII. Cleavage of the oxide ring in tubaic acid.** H. L. Haller and F. B. LaForge (J. Amer. Chem. Soc., 1931, 53, 4400—4408, 4450—4451, 4460—4462).—XVI. The reactions involving the formation of derritol, rotenol, dehydrorotenone, and derrisic acid are explained on the basis of their oxidation products. All these reactions are concerned with the MeO-containing part of the rotenone mol., which is best expressed as (I), where R represents that part of the mol. yielding tubaic acid. The original must be consulted for the arguments advanced.

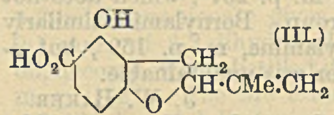

(I.)

Dihydroderritol and $CH_2Br\cdot CO_2Et$ with NaOEt give the Et ester, m. p. 128°, of dihydroderrisic acid. Similarly, *iso*derritol affords the *Et* ester, m. p. 128°, of *iso*derrisic acid (esterified to the same ester), whilst derritol gives dehydrorotenone and Et derrisate.

XVII. Dihydrorotenone exists in dimorphic forms, m. p. 164° and 216°; the former changes into the latter on keeping.

XVIII. A small amount of *tetrahydrotubaic acid* (II), $C_{12}H_{16}O_4$, m. p. 206° (decomp.), is formed in addition to the dihydro-acid when tubaic acid is reduced catalytically. (II) gives a violet colour with $FeCl_3$, forms a Ac_2 derivative, a Me ester Me ether, and is optically inactive. When heated to 210—220°, a *phenol*, $C_{11}H_{16}O_2$, m. p. 85°, probably 2-iso*amyl*-*resorcinol*, is formed. Tubaic acid is represented as (III), and (II) as 2 : 4-dihydroxy-3-*iso*amylbenzoic acid.

C. J. West (*b*).


(III.)

α-Terpenyl acetate. I. H. Paillard and P. Tempia (Helv. Chim. Acta, 1931, 14, 1314—1317).—α-Terpenyl acetate (I) is best obtained pure by Houben's method (A., 1906, i, 440). Boulez's method (A., 1907, ii, 306) also gives good results; the *m*-xylene can be replaced by turpentine. (I) is not obtained from α-pinene and AcOH in presence of H_2SO_4 (G.P. 67,255) or $PhSO_3H$ (Barbier and Grignard, A., 1908, i, 94).

H. Burton.

Reducing action of magnesium bornyl chloride. I. R. Sherwood and W. F. Short (J.C.S., 1931, 3340).—Ethereal Mg bornyl chloride reduces *iso*valeraldehyde, citral, and piperitone to *iso*amyl alcohol, geraniol, and phellandrene, respectively, together with small amounts of borneol (3 : 5-*dinitrobenzoate*, m. p. 154·5°) in each case.

J. W. Baker.

Catalytic production of camphor from borneol. P. P. Schorigin and Y. Makarov-Semlianski (J. Appl. Chem., Russia, 1931, 4, 69—75).—Borneol, C_6H_6, H_2O, and air react at 300° in presence of active V_2O_5; the yield is 80% of the theoretical, 50% of the borneol being recovered. Camphane is formed if the optimal conditions are not observed. When borneol and C_6H_6 are passed over finely-divided Cu or bronze at 255°, H_2 is eliminated and 86—88% of camphor is obtained, 12—13% of the borneol being recovered.

Chemical Abstracts.

Isomerisation of linalool into camphor. (Mlle.) I. K. Vinogradova (J. Gen. Chem. Russ., 1931, 1, 660—667).—*l*-Linalool, when heated with 10—15% of Al and a trace of $HgCl_2$ for 8 hr., gives *dinitrofluorenone*, m. p. above 300° (reduced to a *nitroaminofluorenone*, m. p. 243—244°, by Na_2S), and 2-nitrofluorenone; cold, fuming HNO_3 gives a similar unstable substance, which forms 2 : 7-dinitrofluorenone on oxidation. *O*-Acetylfluorenoneoxime and conc. HNO_3 in Ac_2O at 30—40° give the 2-*nitro*-compound, m. p. 228°, hydrolysed by KOH or conc. H_2SO_4 to 2-*nitrofluorenoneoxime*, m. p. 249° (decomp.), which was prepared also from 2-nitrofluorenone, which it yields on oxidation by $Na_2Cr_2O_7$ in AcOH.

R. S. CAHN.

Haloform reaction. IV. Influence of *o*-methoxy-groups. R. C. FUSON, M. W. FARLOW, and C. J. STEHMAN (J. Amer. Chem. Soc., 1931, **53**, 4097—4103).—In no case has it been found possible to isolate the trihalogenomethyl intermediate using acetophenones with only one *o*-substituent. 2 : 4 : 6-Trimethoxyacetophenone and NaOBr in dil. or conc. alkali give $\alpha\alpha\alpha$-*tribromo*-2 : 4 : 6-*trimethoxyacetophenone*, m. p. 102·5—103° (corr.), in 67% and 58% yields, respectively; reaction is about 6 times as fast in dil. alkali. The Cl_3-derivative, m. p. 119—120° (corr.), results in 68% yield. Both halogeno-compounds are oxidised to 2 : 4 : 6-trimethoxybenzoic acid by alkali. 2-Methoxyacetonaphthone and NaOBr in H_2O or in 20% EtOH give 51 or 64% of 2-*methoxy*-1-*tribromoacetylnaphthalene*, m. p. 136·5—137° (corr.) (the 1-*trichloroacetyl* derivative has m. p. 131—131·5°), converted by alkali into 2-methoxy-α-naphthoic acid. The retardation of the haloform reaction is of the same order of magnitude in both cases. Since the effect observed with 2 : 1-$OMe{\cdot}C_{10}H_6Ac$ is to be ascribed to the combined influences of the OMe and the benzo-groups, it is evident that the separate effect of the benzo-group is similar to that of the OMe group.

C. J. WEST (*b*).

Action of Grignard solutions on 10-methoxyanthrones. E. DE B. BARNETT (J.C.S., 1931, 3340—3341).—10-Methoxyanthrone (prep. improved) interacts with $CH_2Ph{\cdot}MgCl$ in the cold to form anthraquinone, 10 : 10′-dimethoxy-10 : 10′-dianthrone, and 10-*methoxy*-9-*benzyl*-9 : 10-*dihydroanthranol*, m. p. 129°, which with HCl and AcOH gives 10-chloro-9-benzylanthracene. 10-Methoxy-1 : 4-dimethylanthrone with MgMeI (3 mols.) gives 10-*methoxy*-1 : 4 : 9-*trimethyl*-9 : 10-*dihydroanthranol*, m. p. 148°, but this did not give a definite product with HCl–AcOH. A poor yield of 10-phenyl-1 : 4-dimethylanthrone was obtained with PhMgBr, and $CH_2Ph{\cdot}MgCl$ and Mg *o*-tolyl bromide gave only resinous products.

H. A. PIGGOTT.

Chemical participation of water in the oxidising action of *p*-benzoquinone; theory of oxidative processes. A. BACH and K. NIKOLAIEV (Ber., 1931, **64**, [*B*], 2769—2772).—In absence of H_2O there is no reaction between *p*-benzoquinone and EtOH when irradiated; reaction increases with increasing amounts of H_2O, although there is no direct proportionality. The presence of H_2O is essential for the oxidation by *p*-benzoquinone of pyrogallol in EtOH, $COMe_2$, or Et_2O or of *p*-phenylenediamine in Et_2O. It is considered that H_2O has a somewhat stabilising effect on the peroxide form of *p*-benzoquinone owing to the formation of *p*-hydroxyphenyl H peroxide, which imparts its active O to the substrate and is therefore deoxidised to quinol. H. WREN.

Complex salts of hydroxyquinones. I. A. MANGANI (Gazzetta, 1931, **61**, 820—826).—The *Na* salt of 2-hydroxy-α-naphthaquinone, *Co*, *Mg*, and *Zn* salts of 5-hydroxy-α-naphthaquinone, and *Co* and *Zn* salts of naphthazarin, which are probably additive compounds with Co and Zn acetates, are described. Chrysazin (1 : 8-dihydroxyanthraquinone) forms *hydrogen Co*, *Mg*, *Zn*, and *Cu* salts, the last being a very sensitive test, and a neutral *Co* salt.

E. E. J. MARLER.

Hydroxyanthraquinones. I. Synthesis of purpurin. P. G. MARSHALL (J.C.S., 1931, 3206—3208).—Quinizarin heated with Na_2SO_3 and CuO in H_2O gives an almost quant. yield of the 2-sulphonic acid (I); the Na salt when heated with $Ca(OH)_2$ and H_2O at 250° affords purpurin (84% yield). Zimmermann's method (A., 1930, 941) of prep. of (I) does not give exclusively the 2-sulphonic acid. H. BURTON.

Anthrone series. III. Synthesis of 3-methoxyphthalaldehydic acid and a new synthesis of chrysazin. IV. Synthesis of the anthrones derived from chrysophanic acid. C. A. NAYLOR, jun. [with J. H. GARDNER] (J. Amer. Chem. Soc., 1931, **53**, 4109—4113, 4114—4119).—III. Oxidation of 1 : 5-dimethoxynapththalene with alkaline $KMnO_4$ gives 11—16% of 3-*methoxyphthalaldehydic acid* (I), m. p. 121—122° to a turbid liquid, which then partly solidifies and re-melts at 144·8°; all m. p. are corr. *p*-$C_6H_4Br{\cdot}OH$ and (I) with 85% H_2SO_4 afford 55% of 3-*methoxy*-2-(5-*bromo*-2-*hydroxyphenyl*)*phthalide*, m. p. 198—200°, reduced by Zn and 10% NaOH to 3-*methoxy*-2-o-*hydroxybenzylbenzoic acid*, m. p. 185—186°, which is converted by conc. H_2SO_4 at room temp. into 1-*hydroxy*-8-*methoxy*-10-*anthrone*, m. p. 170—171°. This is oxidised by CrO_3 in AcOH to 1-hydroxy-8-methoxyanthraquinone (chrysazin Me ether), demethylated to chrysazin (11% yield) (Ac_2 derivative, m. p. 231—232°).

IV. 6-Bromo-*m*-cresol and (I) with 85% H_2SO_4 give 3-*methoxy*-2-(5-*bromo*-2-*hydroxy*-4-*methylphenyl*)*phthalide*, m. p. 243—244·6°, convertible (as above) into 3-*methoxy*-2-(2′-*hydroxy*-4′-*methylbenzyl*)*benzoic acid*, m. p. 164—164·6°, and 1-*hydroxy*-8-*methoxy*-3-*methyl*-10-*anthrone* (II), m. p. 173·8—175°. Demethylation of 1-*hydroxy*-8-*methoxy*-3-*methylanthraquinone*, m. p. 202—204°, gives chrysophanic acid (III), identical with the acid prepared by Eder and Widmer's method (A., 1922, i, 260; 1923, i, 688). Reduction of (III) with Sn and conc. HCl in AcOH affords 1 : 8-*dihydroxy*-3-*methyl*-9-*anthrone*, m. p. 203·4—204° (corresponding anthranyl *acetate*, m. p. 236—237°, identical with a product obtained by successive demethylation and acetylation of chrysarobin). Demethylation of (II) gives 1 : 8-*dihydroxy*-3-*methyl*-10-*anthrone*, m. p. 179—180° (corresponding anthranyl *acetate*, m. p. 209—210°), also obtained from 3-*hydroxy*-2-(2′-*hydroxy*-4′-*methylbenzyl*)*benzoic acid*, m. p. 157—158°, which is prepared by reducing the corresponding benzoylbenzoic acid with Zn and aq. NH_3.

C. J. WEST (*b*).

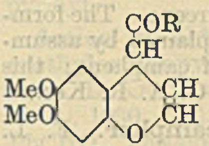
Hydroxy-derivatives of retene. L. F. FIESER and M. N. YOUNG (J. Amer. Chem. Soc., 1931, **53**, 4120—4129).—The C_2 and C_3 atoms of phenanthrene are joined by a single linking and a 2(or 3)-phenanthrol cannot, therefore, couple with diazonium salts if the 1(or 4)-position is substituted, since a double linking is required for the formation of the intermediate additive compound. Using this principle, reduction potential data, and the Dimroth test for α-hydroxyquinones, it is shown that the hydroxyretenes described by Komppa and Wahlforss (A., 1931, 226) are 2-, m. p. 200—202°, and 6-retenols, m. p. 161—162°. Oxidation of 6-acetoxyretene with CrO_3 in AcOH gives 6-*acetoxyretenequinone*, m. p. 200°, hydrolysed by EtOH–KOH to 6-*hydroxyretenequinone* (*Me ether*, m. p. 196°, also prepared by oxidation of 6-*methoxyretene*, m. p. 115—116°). 6-Retenol and p-$NO_2\cdot C_6H_4\cdot N_2Cl$ in AcOH afford 5-p-*nitrobenzeneazo-6-retenol*, decomp. when heated, which could not be reduced smoothly. The Na salt of the dye obtained from diazobenzenesulphonic acid is readily reduced, but the 5-amino-6-retenol could not be obtained pure; the crude amine, Ac_2O, and NaOAc give an *oxazole*, m. p. 112°. Retene-6-sulphonic acid is characterised as the p-*toluidine* salt. 1-*Chlorophenanthraquinone*, m. p. 217—218°, is prepared in poor yield from the 1-sulphonate and $KClO_3$ in HCl; 6-chlororetenequinone could not be obtained by this method. 2-*Acetoxyretene* and 2-*acetoxyretenequinone* have m. p. 160° and 171—172°, respectively. 2-*Hydroxyretenequinone*, m. p. 229—231°, gives a bluish-green coloration with cold, dil. EtOH–alkali changing to reddish-brown when heated. This colour change is reversible and is also shown by phenanthraquinones containing a *m*-OH group to one of the CO groups. Reduction of retenequinone with Zn and AcOH gives 9-*retenol* (I), m. p. 176° (*Me ether*, m. p. 108°; 10-p-*nitrobenzeneazo*-derivative, m. p. 243·5—244·5°), isolated through its *acetate*, m. p. 141°. When a solution of (I) in AcOH is exposed to air for 3 days, a mol. *compound*, m. p. 160—161°, of (I) and retenequinone is obtained. 9-*Acetoxy*-10-*allylretene*, m. p. 102°, is obtained by rearrangement of 9-*allyloxyretene*, m. p. 84°, and subsequent acetylation. Reduction of 1-methylphenanthraquinone [as in the prep. of (I)] gives 1-*methyl-9-acetoxyphenanthrene*, m. p. 99—100°, whilst the usual reductive acetylation affords the *quinol diacetate*, m. p. 189°. The potentials of retenequinone and its 2- and 6-OH derivatives are 0·421, 0·385, and 0·348 volts, respectively.

[With H. D. Newman.] The following compounds are described: 2-*allyloxyphenanthrene*, m. p. 92°; 1-*allyl*-2-*phenanthrol*, m. p. 125·5° (*acetate*, m. p. 105°; *coumaran* derivative, m. p. 155°; *allyl ether*, m. p. 91·5°); 4-*allyl*-3-*phenanthrol*, m. p. 91° (*acetate*, m. p. 56°; *coumaran* derivative, m. p. 89°).

C. J. West (*b*).

Manufacture of aminodiazoanthraquinones and of anthraquinone derivatives therefrom. I. G. Farbenind. A.-G.—See B., 1932, 57.

Rotenone. XVI. Interpretation of characteristic reactions of rotenone. F. B. LaForge, H. L. Haller, and L. E. Smith. **XVII. Dimorphic forms of dihydrorotenone.** F. B. LaForge and G. L. Keenan. **XVIII. Cleavage of the oxide ring in tubaic acid.** H. L. Haller and F. B. LaForge (J. Amer. Chem. Soc., 1931, 53, 4400—4408, 4450—4451, 4460—4462).—XVI. The reactions involving the formation of derritol, rotenol, dehydrorotenone, and derrisic acid are explained on the basis of their oxidation products. All these reactions are concerned with the MeO-containing part of the rotenone mol., which is best expressed as (I), where R represents that part of the mol. yielding tubaic acid. The original must be consulted for the arguments advanced.



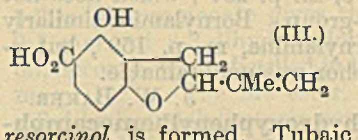
(I.)

Dihydroderritol and $CH_2Br\cdot CO_2Et$ with NaOEt give the Et ester, m. p. 128°, of dihydroderrisic acid. Similarly, *iso*derritol affords the *Et* ester, m. p. 128°, of *iso*derrisic acid (esterified to the same ester), whilst derritol gives dehydrorotenone and Et derrisate.

XVII. Dihydrorotenone exists in dimorphic forms, m. p. 164° and 216°; the former changes into the latter on keeping.

XVIII. A small amount of *tetrahydrotubaic acid* (II), $C_{12}H_{16}O_4$, m. p. 206° (decomp.), is formed in addition to the dihydro-acid when tubaic acid is reduced catalytically. (II) gives a violet colour with $FeCl_3$, forms a Ac_2 derivative, a Me ester Me ether, and is optically inactive. When heated to 210—220°, a *phenol*, $C_{11}H_{16}O_2$, m. p. 85°, probably 2-iso*amyl-resorcinol*, is formed. Tubaic acid is represented as (III), and (II) as 2 : 4-dihydroxy-3-*iso*amylbenzoic acid.

C. J. West (*b*).



(III.)

α-Terpenyl acetate. I. H. Paillard and P. Tempia (Helv. Chim. Acta, 1931, 14, 1314—1317).—α-Terpenyl acetate (I) is best obtained pure by Houben's method (A., 1906, i, 440). Boulez's method (A., 1907, ii, 306) also gives good results; the *m*-xylene can be replaced by turpentine. (I) is not obtained from α-pinene and AcOH in presence of H_2SO_4 (G.P. 67,255) or $PhSO_3H$ (Barbier and Grignard, A., 1908, i, 94).

H. Burton.

Reducing action of magnesium bornyl chloride. I. R. Sherwood and W. F. Short (J.C.S., 1931, 3340).—Ethereal Mg bornyl chloride reduces *iso*valeraldehyde, citral, and piperitone to *iso*amyl alcohol, geraniol, and phellandrene, respectively, together with small amounts of borneol (3 : 5-*dinitrobenzoate*, m. p. 154·5°) in each case.

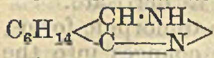
J. W. Baker.

Catalytic production of camphor from borneol. P. P. Schorigin and Y. Makarov-Semlianski (J. Appl. Chem., Russia, 1931, 4, 69—75).—Borneol, C_6H_6, H_2O, and air react at 300° in presence of active V_2O_5; the yield is 80% of the theoretical, 50% of the borneol being recovered. Camphane is formed if the optimal conditions are not observed. When borneol and C_6H_6 are passed over finely-divided Cu or bronze at 255°, H_2 is eliminated and 86—88% of camphor is obtained, 12—13% of the borneol being recovered.

Chemical Abstracts.

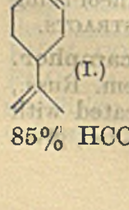
Isomerisation of linalool into camphor. (Mlle.) I. K. Vinogradova (J. Gen. Chem. Russ., 1931, 1, 660—667).—*l*-Linalool, when heated with 10—15% of Al and a trace of $HgCl_2$ for 8 hr., gives

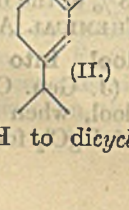
30% of dipentene, traces of myrcene or linaloolene, 2% of camphor, 0·8% of borneol, 22% of dimyrcene, 8·5% of H_2O, and 15% of tar; all these products are inactive or dextrorotatory. Geraniol on similar treatment gives only dipentene and dimyrcene. The formation of borneol and camphor is explained by assuming the intermediate production of camphene; this was not isolated. G. A. R. Kon.

Derivatives of phenylaminocamphor. F. L. Rose (J.C.S., 1931, 3337—3339).—Aminocamphor (best prepared by electrolytic reduction of oximinocamphor) and 2 : 4-dinitrochlorobenzene yield 2 : 4-dinitroanilinocamphor, m. p. 204°, $[\alpha]_D$ $-120·3°$ in $CHCl_3$, in which attempts to reduce only one NO_2-group were unsuccessful, but which with $SnCl_2$ and HCl affords *aminocamphanodihydroquinoxaline*,  $C_6H_{14}<\begin{smallmatrix}CH\cdot NH\\ C\!=\!=\!=\!=N\end{smallmatrix}>C_6H_3\cdot NH_2$ (I), m.p. 189°, $[\alpha]_D$ $+41·9°$ in EtOH (*Ac*$_2$, m. p. 220°, *Bz*, m. p. 227°, derivatives), the $(NH_2)_2$-compound being formed intermediately. With MeI at 100° (I) affords a mixture of the yellow *methiodide* (insol. in $CHCl_3$) and the red *hydriodide* of *methylaminocamphanodihydroquinoxaline* (*nitrosoamine*). With 2 : 4-dinitrochlorobenzene (I) gives a *dinitrophenyl* derivative, m. p. 237°, which does not contain a primary NH_2-group. Bornylamine similarly gives dinitrophenylbornylamine, m. p. 159°, but *o*-nitrophenylaminocamphor was unobtainable. J. W. Baker.

Identification of hydroxyphenylhomocampholic acid. L. Palfray (Bull. Soc. chim., 1931, [iv], **49**, 1529—1540; cf. A., 1924, i, 854).—With 1 mol. of BzCl, sodiocamphor gives only dibenzoylcamphor and not the monobenzoyl derivative. By using 2 mols. of $NaNH_2$ in PhMe, heating for 6 hr. to eliminate NH_3, and adding 1 mol. of BzCl the yield of dibenzoylcamphor is appreciably raised; with a further mol. of BzCl at 110°, tribenzamide, m. p. 202°, is also formed and a smaller amount of dibenzoylcamphor. The latter is converted into 1-hydroxy-2-benzoylcamphene by boiling aq. alcoholic alkali. With NaOEt at 160—170° dibenzoylcamphor affords 92% of 1-hydroxy-2-benzoylcamphene and BzOH with some benzoylcampholic acid, m. p. 163°; at 200—220° a 72% yield of (impure) benzoylcampholic acid is obtained. Hydroxybenzoylcamphene is only partly hydrolysed by alcoholic NaOH, yielding 60% of benzoylcampholic acid at 200—220°, and is not attacked by fused Na *p*-tolyloxide at 200—220°. Phenylhydroxyhomocampholic acid, m. p. 202—203°, $[\alpha]_D^{18·5}$ $+73° 22'$ (Me ester, m. p. 104—105°), and BzCl give benzylidenecamphor, m. p. 96°. R. Brightman.

Polyterpenes and polyterpenoids. LXII. Constitution of *cyclo*isoprenemyrcene. L. Ruzicka and W. Bosch (Helv. Chim. Acta, 1931, **14**, 1336—1339).—*cyclo*Isoprenemyrcene (Semmler and Jonas, A., 1913, i, 742), b. p. 136—139°/14 mm., when regenerated from its trihydrochloride, m. p. 81° (cf. *loc. cit.*), is considered to be (I), since it is cyclised by 85% HCO_2H to di*cyclo*isoprenemyrcene (II), b. p. 130—134°/13 mm., which is dehydrogenated by Se at 320° to eudalene. H. Burton.


(I.)


(II.)

3-Methylfuran. I. J. Rinkes (Rec. trav. chim., 1931, **50**, 1127—1132).—Et 3-carbethoxy-4-methyl-2-furylacetate (A., 1899, i, 675) is converted by NaOEt and amyl nitrite in EtOH into the *oximino*-derivative, m. p. 82°, which when heated with aq. H_2SO_4 gives 2-*cyano*-4-*methylfuran*-3-*carboxylic acid*, m. p. 203—204°, decarboxylated by quinoline and Cu-bronze at 210—220° to 2-*cyano*-4-*methylfuran*; this is hydrolysed by KOH in aq. MeOH to 4-*methylfuran*-2-*carboxylic acid*, m. p. 129°, which is partly decomposed at 200° into CO_2 and 3-methylfuran, b. p. 65—66°.

3 : 6-*Endoxo*-4-*methyl*-, m. p. 82°, and -3-*methyl*-Δ^4-*tetrahydrophthalic anhydride*, m. p. 80°, are obtained by interaction of 3- and 2-methylfuran, respectively, with maleic anhydride. H. A. Piggott.

Synthesis of 3-methylfuran. T. Reichstein and H. Zschokke (Helv. Chim. Acta, 1931, **14**, 1270—1276).—Et 3-carbethoxy-4-methyl-2-furylacetate, b. p. 109—110°/0·5 mm., produced with the corresponding pyrrole from Et acetonedicarboxylate, chloroacetone, and NH_3 in Et_2O, is converted by Et nitrite in presence of dry NaOEt and Et_2O into *Et* 3-*carbethoxy*-4-*methyl*-2-*furyloximinoacetate*, m. p. 83—84° (all m. p. are corr.). The free *oximino-dicarboxylic acid*, m. p. 187—191° (decomp.), and Ac_2O give 2-*cyano*-4-*methylfuran*-3-*carboxylic acid* (I), m. p. 195—199°, which with quinoline and Cu-bronze at 220° affords 2-*cyano*-4-*methylfuran*, b. p. 57—58°/12 mm., hydrolysed to 4-*methylfuroic acid*, m. p. 131—132°. The oximino-acid and NH_2OH,HCl give (I) and 3-*carboxy*-4-*methylfuran*-2-*carboxylamide*, m. p. 228—230°, hydrolysed to 4-*methylfuran*-2 : 3-*dicarboxylic acid*, m. p. 233° (decomp.), which when heated alone passes into 4-*methylfuran*-3-*carboxylic acid*, m. p. 138—139°. The dicarboxylic acid with quinoline and Cu-bronze at 270—290° gives 3-methylfuran. H. Burton.

Derivatives in the tetrahydrofuran series. R. Paul (Compt. rend., 1931, **193**, 1428—1430).—The action of powdered K in Et_2O on δε-dibromopentanol affords some δ-bromo-Δ^δ-pentenol and chiefly 2-*bromomethyltetrahydrofurfan*, b. p. 67°/18 mm., which can be converted through the *acetate*, b. p. 93—94°/22 mm., into 2-tetrahydrofurfuryl alcohol. It is suggested that a positive charge on the δ-C atom causes 5-ring formation. F. R. Shaw.

Aldehyde syntheses in the furan series. II. Synthesis of elsholtzic [3-methylfuroic] acid and elsholtzia [3-methyl-2-furyl *iso*butyl] ketone. T. Reichstein, H. Zschokke, and A. Goerg (Helv. Chim. Acta, 1931, **14**, 1277—1283; cf. Asahina *et al.*, A., 1924, i, 976).—2 : 4-Dimethylfuran is converted by the method previously described (A., 1930, 783) into 3 : 5-*dimethylfurfuraldehyde*, b. p. about 78°/13 mm. [*semicarbazone*, m. p. 220—221° (decomp.)], oxidised by Ag_2O in aq. EtOH–NaOH to 3 : 5-*dimethylfuroic acid*, m. p. 146—147° (corr.). 3-Methylfuran is similarly converted into 3-*methylfurfuraldehyde*, b. p. 60—61°/12 mm. [*semicarbazone*, m. p. 216—218° (decomp.)], and thence into 3-methylfuroic acid [amide, m. p. 90—90·5° (lit. 85—86°)]. 3-*Methylfurfuraldoxime*, m. p. 73—76°, and Ac_2O give 2-*cyano*-3-*methyl*-

furan, b. p. 54·5—55°/12 mm., m. p. about 19°, which with $MgBu^{\beta}Br$ affords 3-methyl-2-furyl Bu^{β} ketone.
H. BURTON.

Exhaustive *O*-methylation of quercetin. A. S. GOMM and M. NIERENSTEIN (J. Amer. Chem. Soc., 1931, **53**, 4408—4411).—Quercetin and diazomethane in dioxan give 3 : 7 : 3′ : 4′-tetramethylquercetin, m. p. 159—160° (Ac derivative, m. p. 169—170°), previously supposed to be the 7 : 3′ : 4′-Me_3 derivative (Waliaschko, A., 1909, i, 248; cf. Wunderlich, A., 1908, i, 559), converted by Me_2SO_4 and solid KOH into the Me_5 derivative, m. p. 151—152°. C. J. WEST (*b*).

Ring closure studies in the piperidine series. G. R. CLEMO, J. ORMSTON, and G. R. RAMAGE (J.C.S., 1931, 3185—3190).—Et piperidine-3-carboxylate (I), $CH_2Cl{\cdot}CO_2Et$, and anhyd. K_2CO_3 at 100° (bath) give *Et 3-carbethoxypiperidinoacetate* (II), b. p. 125°/0·1 mm. (*dihydrazide*, m. p. 162°; *diamide*, m. p. 213°, distils unchanged), hydrolysed by dil. HCl to *3-carboxypiperidinoacetic acid*, m. p. 270° (*Cu* salt). Piperidine and β-cyanoethyl *p*-toluenesulphonate (III) at 130° afford *β-piperidinopropionitrile*, b. p. 116°/18 mm. (*methiodide*, m. p. 155°), whilst (I) and (III) give β-3-*carbethoxypiperidinopropionitrile*, b. p. 133°/0·1 mm., converted by EtOH–HCl into *Et* β-3-*carbethoxypiperidinopropionate*, b. p. 130°/0·1 mm. (free *acid*, m. p. 195—196°; *dihydrazide*, m. p. 152°), also prepared from (I), $CH_2Cl{\cdot}CH_2{\cdot}CO_2Et$, and NaOAc. The last-named ester and (II) do not undergo the Dieckmann reaction and ring closure could not be effected by distillation of the Th salts of the corresponding acids. γ-3-*Carbethoxypiperidinobutyronitrile*, b. p. 135°/0·1 mm., from (I), $CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CN$, and K_2CO_3, is converted by EtOH–HCl into *Et* γ-3-*carbethoxypiperidinobutyrate* (IV), b. p. 133°/0·1 mm. (*dihydrazide*, m. p. 165°); distillation of the Th salt of the free acid gives a basic, non-ketonic oil, b. p. 105—110°/20 mm. Ring closure of 3-*carbethoxypiperidinoacetone*, b. p. 110°/0·1 mm., from (I), bromoacetone, and K_2CO_3, could not be effected. The quaternary *salt*, m. p. 139°, from (IV) and Me *p*-toluenesulphonate when treated with Na in boiling PhMe, and then hydrolysed with HCl, gives a little basic, non-ketonic oil, b. p. 70°/0·3 mm.
H. BURTON.

Electron-sharing ability of organic radicals. Nitrogen heterocycles. L. C. CRAIG and R. M. HIXON (J. Amer. Chem. Soc., 1931, **53**, 4367—4732).—The relationship previously demonstrated (A., 1927, 814; 1930, 1525, 1526) between the electron-sharing ability of the org. radicals and the affinities of the polar groups in the series $R{\cdot}NH_2$, $R{\cdot}CO_2H$, $R{\cdot}[CH_2]_x{\cdot}CO_2H$, and R·HgX has been shown to hold for both the 2- and *N*-substituted pyrrolidines. 2-*Aminomethylpyridine* (I), b. p. 91°/15 mm. [*oxalate*, m. p. 167°; *chloroaurate*, m. p. 204° (decomp.); *chloroplatinate*], and 3-*aminomethylpyridine* (II), b. p. 112°/18 mm. (*chloroplatinate*, not melted at 320°; *picrate*, m. p. 211°), are prepared by reduction of the corresponding pyridylformaldoximes with Zn dust and AcOH. The following dissociation consts. are reported: pyrrolidine, $1{\cdot}3\times10^{-3}$; *N*-*cyclo*hexyl-, $5{\cdot}0\times10^{-4}$; *N*-butyl-, $2{\cdot}3\times10^{-4}$; *N*-methyl-, $1{\cdot}5\times10^{-4}$; *N*-benzyl-, $3{\cdot}2\times10^{-5}$; *N*-*p*-tolyl-, 5×10^{-10}; *N*-phenyl-, 2×10^{-10}; 2-ethyl-, $2{\cdot}7\times10^{-4}$; 2-phenyl-, 4×10^{-5}; β-pyridyl-α-*N*-methylpyrrolidines, 9×10^{-7}; *meta*nicotine, 9×10^{-5}; 2-ethylpyrroline, $2{\cdot}7\times10^{-7}$; 2-pyrrylmethylamine, 9×10^{-6}; (II), $1{\cdot}1\times10^{-6}$; (I), 1×10^{-6}. The 2-pyrryl radical is more negative than Ph, but is less negative than pyridyl. C. J. WEST (*b*).

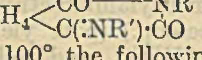
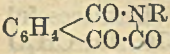
Action of aldehydes on 2-amino- and 2-dimethylaminopyridine. A. E. TSCHITSCHIBABIN and I. L. KNUNJANZ (Ber., 1931, 64, [*B*], 2839—2842; cf. A., 1930, 221).—2-Aminopyridine is converted by PhCHO, anisaldehyde, and piperonal in boiling HCO_2H, respectively, into 2-benzylamino-, m. p. 94°, 2-p-*methoxybenzylamino*-, m. p. 128°, and 2 : 3′ : 4′-*methylenedioxybenzylamino*-, m. p. 99—100°, -*pyridine*. 2-*Formamidopyridine* has m. p. 71°. 2-Dimethylaminopyridine, PhCHO, and anhyd. $ZnCl_2$ at 230—240° afford *phenyldi-2-dimethylamino-5-pyridylmethane*, m. p. 130—131°, readily oxidised by PbO_2 to the corresponding *carbinol*, m. p. 123—124°, which does not yield true dyes with acids. *o*-Nitrobenz- and salicyl-aldehydes do not react with 2-aminopyridine. H. WREN.

Strychnine and brucine. XIII. Dihydroindolylpropionic and dihydroindolylbutyric acids. B. K. BLOUNT and R. ROBINSON (J.C.S., 1931, 3158—3160).—Catalytic reduction (PtO_2) of Et β-3-indolylpropionate gives the *Et* ester, b. p. 145°/0·1 mm., of β-3-dihydroindolylpropionic acid (I), an oil, decomp. when distilled in high vac. (*Bz* derivative, m. p. 152°). The *Me* ester, b. p. 160°/0·1 mm., of γ-3-dihydroindolylbutyric acid (II), a resin (1-p-*nitrobenzoyl* derivative, m. p. 163—164°), is prepared similarly from Me γ-3-indolylbutyrate. (I) and (II) show no tendency to form cyclic amides. Strychnic acid is not regarded as a substituted derivative of (I) or (II) (cf. Leuchs, A., 1931, 242). H. BURTON.

Attempts to find new antimalarials. VI. Derivatives of 2-β-aminoethylquinoline. W. O. KERMACK and W. MUIR. **VII. Quinoline compounds having in the 4-position a side-chain containing two or more nitrogen atoms.** W. O. KERMACK and J. F. SMITH (J.C.S., 1931, 3089—3096, 3096—3104).—VI. Et β-2-quinolylpropionate and N_2H_4 hydrate at 140° give β-2-*quinolylpropionhydrazide*, m. p. 165°, converted by HNO_2 into s-*di*-(β-2-*quinolylpropion*)*hydrazide*, m. p. 265°. 2-Methylquinoline hydrochloride (1 mol.), 40% CH_2O (2 mols.), and piperidine (2 mols.) at 100° (bath) afford 2-β-piperidinoethylquinoline, decomp. on attempted distillation (isolated in 72% yield as the *picrate*, m. p. 155°). 2-β-Diethylamino- [picrate, m. p. 123—124° (33% yield)] and 2-β-phenylmethylamino-ethylquinoline [*picrate*, m. p. 175° (decomp.) (poor yield)] are prepared similarly, using $NHEt_2$ and NHPhMe, respectively, instead of piperidine. Unsuccessful attempts were made to substitute MeCHO for CH_2O in these reactions. α-Piperidino-β-methylbutan-γ-one (I) (A., 1928, 299) and $o\text{-}NH_2{\cdot}C_6H_4{\cdot}CHO$ (II) in aq. EtOH–NaOH give 2-β-piperidino*iso*propylquinoline [*picrate*, m. p. 167—168°; *dipicrate* (?), m. p. 201°] and 2 : 3-dimethylquinoline; the last-named is probably formed from (II) and COMeEt, which arises by hydrolysis of (I). Similarly, 2-piperidinomethyl*cyclo*hexanone and (II) afford 1-piperidinomethyl-1 : 2 : 3 : 4-tetrahydroacridine (*picrate*, m. p. 206°), whilst 2-diethylaminomethyl*cyclo*hexanone and (II) give an amorphous *compound*, $C_{14}H_{17}O_2N$, m. p. 65—75°.

VII (cf. A., 1930, 1048). Piperidine, *N*-β-bromoethylphthalimide (III), and anhyd. K_2CO_3 in boiling PhMe give N-β-*piperidinoethylphthalimide*, m. p. 91°, hydrolysed (N_2H_4 hydrate method) to β-piperidinoethylamine (IV), decomp. when heated in vac. [*picrate*, m. p. 225° (decomp.)]. (IV), 4-chloro-6-methoxy-2-methylquinoline (V), and a trace of Cu-bronze at 100—120° afford 4-β-*piperidinoethylamino-6-methoxy-2-methylquinoline* (+$2H_2O$), m. p. 73°, m. p. (anhyd.) 140—141°, which has no antimalarial action. The *oxime*, m. p. 91—92°, of α-piperidinobutan-γ-one is reduced by Zn dust and EtOH–AcOH to γ-amino-α-piperidinobutane (poor yield), b. p. 106—110°/12 mm. [*hydrochloride*, m. p. 210°; *dihydrochloride*, m. p. 241°; *dipicrate*, m. p. 241—242° (decomp.)], which could not be condensed with (V) or 4-bromo-6-methoxy-2-methylquinoline (VI). Piperazine hexahydrate and (III) at 140—150° give *N*-β-piperazinoethylphthalimide [*dihydrobromide*, m. p. 243° (decomp.)] and 1 : 4-*di*-(β-*phthalimidoethyl*)*piperazine*, m. p. 240° (*dihydrobromide*, m. p. 300°), hydrolysed to β-piperazinoethylamine (*dipicrate*, m. p. 290°) and 1 : 4-di-(β-aminoethyl)piperazine (VII) [*tetrahydrochloride*, m. p. 295° (decomp.)], respectively. Extraction of a strongly alkaline EtOH solution of (VII) with $CHCl_3$ [during a prep. by a modification of Franchimont and Kramer's method (A., 1912, i, 391)] resulted in the formation of 1 : 4-di-(β-iso*cyanoethyl*)-*piperazine*, m. p. 280° [*dihydrochloride*, m. p. 277° (decomp.)]. (VI) and (VII) at 170° give 4-(4′-β-aminoethylpiperazinoethylamino)-6-methoxy-2-methylquinoline [*picrate* (+$3H_2O$), m. p. 175°] and 1 : 4-di-(β-6′-methoxy-2′-methyl-4′-quinolylaminoethyl)piperazine [*tetrahydrochloride* (+$5H_2O$), m. p. above 310°]; the last-named is obtained in better yield when an excess of (VI) is used. The Cl atom in 4-(4′-chloroacetylpiperazino)-6-methoxy-2-methylquinoline [*hydrochloride*, m. p. 256° (decomp.); unstable *picrate*, m. p. 155—160°], prepared from the 4-piperazino-derivative (*loc. cit.*) and $CH_2Cl\cdot COCl$, is relatively inactive. α-Piperidinobutan-γ-one hydrochloride is apparently dehydrated by $CH_2Cl\cdot COCl$ (not by AcCl) in $CHCl_3$ to the *dihydrochloride*, m. p. 182°, of αη-dipiperidino-γ-keto-ε-methyl-Δ^δ-heptene or αε-dipiperidino-β-acetyl-γ-methyl-Δ^β-pentene.

H. BURTON.

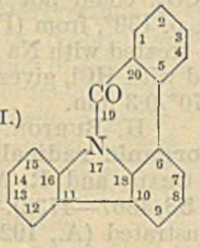
Phthalone-imides and their derivatives. A. MEYER and R. VITTENET (Compt. rend., 1931, 193, 1095—1098).—By hydrolysis of azomethines of the type  $C_6H_4{<}\begin{matrix}CO\text{——}NR\\ C(:NR')\cdot CO\end{matrix}$ (A., 1931, 1414) with dil. HCl at 100° the following α-ketohomophthalimides,  $C_6H_4{<}\begin{matrix}CO\cdot NR\\ CO\cdot CO\end{matrix}$, have been obtained: imide, m. p. 228—229° [lit., m. p. 220—224°; *phenylhydrazone*, m. p. 269—263° (?); *phenylmethylhydrazone*, m. p. 242·5°; *oxime*, m. p. 242—243°]: *phenyl*-, m. p. 220—221° (*phenylhydrazone*, m. p. 246—247°; *phenylmethylhydrazone*, m. p. 204°; *oxime*, m. p. 224—236°; *semicarbazone*, m. p. 230—231°); p-*tolyl*-, m. p. 238° (*phenylhydrazone*, m. p. 258—259°; *phenylmethylhydrazone*, m. p. 199°; *oxime*, m. p. 241—242°; *semicarbazone*, m. p. 236—237°): α-, m. p. 239—240° (*phenylhydrazone*, m. p. 283—284°; *phenylmethylhydrazone*, m. p. 212°); and β-, m. p. 268—269° (*phenylhydrazone*, m. p. 262—263°; *phenylmethylhydrazone*, m. p. 199—200°), -*naphthyl-imide*.

J. W. BAKER.

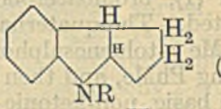
Nitration of carbazole. G. T. MORGAN, J. G. MITCHELL, and (in part) J. R. DOLPHIN (J.C.S., 1931, 3283—3285).—Nitration of carbazole with 60% HNO_3 at 40° raised to 80—90°, or with $BzNO_3$ in dry petroleum at −15° affords mainly 3-nitrocarbazole and the yellow compound, m. p. 164°, which is the main product when Ziersch's conditions (HNO_3 and AcOH; A., 1909, i, 961) are used. This compound is a mol. complex of the 1- and 3-NO_2-derivatives and is separated into its components by fractional sublimation or by addition of EtOH to its solution in NH_2Ph or pyridine, when the 1-NO_2-compound, m. p. 186·5—187·5°, crystallises. This is reduced to 1-aminocarbazole, from which no internal diazoimine could be obtained.

J. W. BAKER.

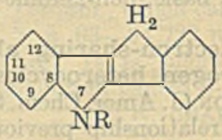
Action of halogens on polycyclic indole derivatives. I. Reaction between bromine and acyl derivatives of tetrahydrocarbazole and benzopentindole. S. G. P. PLANT and M. L. TOMLINSON (J.C.S., 1931, 3324—3337).—9-Acetyltetrahydrocarbazole and Br in CS_2 give an unstable 10 : 11-additive *dibromide*, m. p. 60° (decomp.), converted by H_2O into 10 : 11-*dihydroxy*-9-*acetylhexahydrocarbazole*, m. p. 203°, which is the sole product of bromination in AcOH. Similar bromination of the 9-benzoyl compound affords the 9-Bz derivative (I), m. p. 144—146°, of 11-*hydroxy*-2 : 3 : 4 : 11-*tetrahydrocarbazole* (II), m. p. 115°, which is obtained on hydrolysis with KOH in aq. EtOH and which, with BzCl and KOH, gives, not (I), but the 11-*benzoyloxy*-derivative, m. p. 128°. (I) is formed by elimination of 1 mol. of HBr from the additive dibromide and subsequent hydrolysis of Br to OH, since it is not identical with the 6-Bz derivative, m. p. 107° (by action of BzCl and KOH) of ψ-*indoxyl*spirocyclo*pentane*. When boiled with Ac_2O, (I) affords 19-*ketophenanthrindocoline* (III), m. p. 225° (parent substance has H_2 in place of :O). Similar treatment of (II) affords 2 : 3-*dihydrocarbazole*, m. p. 293—295°. Bromination of 9-phenylacetyl- and 9-cinnamoyl- (improved prep. described) -tetrahydrocarbazole affords 10 : 11-dihydroxy-9-phenylacetylhexahydro- (J.C.S., 1923, **123**, 676), and -9-*cinnamoyl*-2 : 3 : 4 : 11-*tetrahydro*-, m. p. 102—106°, *carbazole*, respectively. Hydrolysis of the latter gives (II), whilst distillation under reduced pressure affords CHPh:CH·CO_2H and carbazole. Bromination of dihydropentindole and of its 8-Ac, -Bz, -CO_2Et, and -*phenylacetyl*, m. p. 116°, derivatives causes development of intense colour, but no definite reaction products could be isolated, but with 8-acetyltetrahydro-



(III.)



(IV.)

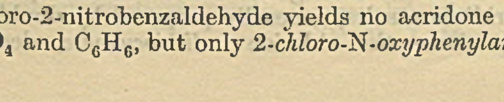


(V.)

pentindole (IV; R=Ac) substitution occurs, giving the 5-*Br*-derivative, m. p. 114°, identical with a specimen prepared from 5-*bromodihydropentindole*, m. p. 140° (by the Fischer indole synthesis from *cyclo*pentanone-*p*-bromophenylhydrazone), by electrolytic reduction to the -*tetrahydro*-compound, m. p. 73°, and subsequent acetylation. Bromination of tetrahydropentindole (IV; R=H) occurs so readily that, even with 1 mol. of Br, the main product, after acetylation, is 5 : 7-*dibromo*-8-*acetyltetrahydropentindole*, m. p. 145°, only a small amount of the 5-*Br*-compound being obtained. Bromination of 7-acetylbenzopentindole (V; R=Ac) gives a mixture (5 : 1) of the 10(or 12)- (VI), m. p. 150°, and 12(or 10)- (VII), m. p. 168°, -*Br*-derivatives (separated by fractional crystallisation from EtOH–$COMe_2$), identical with specimens synthesised by acetylation of the product of the Fischer reaction from α-*hydrindone*-m-*bromophenylhydrazone*, m. p. 118—120°. The corresponding -p-*bromophenylhydrazone*, m. p. 153—159°, similarly affords 11-*bromobenzopentindole*, m. p. 230° (*Ac* derivative, m. p. 174°), but attempts to obtain the 9-bromo-compound from the o-*bromophenylhydrazone* (dimorphous), m. p. 136° (colourless needles, unstable) and m. p. 134° (red prisms), were unsuccessful. Bromination of 7-benzoylbenzopentindole gives only the (10 or 12)-*Br*-derivative, m. p. 193° (converted into the Ac derivative described above), but *Et benzopentindole*-7-*carboxylate*, m. p. 116° ($ClCO_2Et$ and aq. KOH on benzopentindole in $COMe_2$), gives a mixture of *Et* 10(or 12)-, m. p. 166° [converted by hydrolysis and acetylation into (IV)], and 12(or 10)-, m. p. 127° [synthesised by hydrolysis of (VII) and treatment with $ClCO_2Et$], -*bromobenzopentindole*-7-*carboxylate*. J. W. Baker.

ψ-Bases. III. The so-called methylphenylacridol. Activity coefficients of 5-phenyl-10-methylacridinium hydroxide from solubility measurements. J. G. Aston and C. W. Montgomery (J. Amer. Chem. Soc., 1931, 53, 4298—4305; cf. A., 1931, 742).—Hantzsch and Kalb (A., 1900, i, 113) found that the conductivity of a mixture of 5-phenyl-10-methylacridinium sulphate and NaOH fell rapidly with time, and concluded that the change was due to the slow establishment of the equilibrium which, they concluded, was greatly in favour of the ψ-base, phenylmethylacridol. The activity coeffs. of the 5-phenyl-10-methylacridinium hydroxide ψ-basic system have been determined by solubility measurements in dil. solutions of KCl and $BaCl_2$. The vals. are those of a typical strong electrolyte. The solubilities in NH_4Cl and NaOH also show that the base is a strong electrolyte. The interpretation placed on their results by Hantzsch and Kalb appears to be erroneous.
C. J. West (*b*).

Mechanism of the formation of acridones by condensation of *o*-nitrobenzaldehydes with aromatic hydrocarbons. I. Tanasescu and (Mme.) M. Macarovici (Bull. Soc. chim., 1931, [iv], 49, 1295—1303).—Unlike *o*-nitro- and 2 : 4-dinitro-benzaldehyde,

(I.)  (II.)

5-chloro-2-nitrobenzaldehyde yields no acridone with H_2SO_4 and C_6H_6, but only 2-*chloro*-N-*oxyphenylanthranil* (II), m. p. 360—362°, the aldehyde reacting in its tautomeric form (I). With Zn, aq. NH_4Cl, and 95% EtOH the anthranil gives 3-chloroacridone, which, like 2-chlorophenylanthranil *N*-oxide, is converted by dimethylaniline and $POCl_3$ into 3-*chloro*-5-*dimethylanilinoacridine*, m. p. 230—232°, and a *substance*, $C_8H_9O_2N$, m. p. 261°. The same products are obtained from the 3-chloroacridine from 4-chlorodiphenylamine-2-carboxylic acid. The substance, m. p. 168—169°, obtained with 2-nitroacridone in the condensation of 2 : 4-dinitrobenzaldehyde with C_6H_6 is 2 : 4-dinitrobenzophenone. R. Brightman.

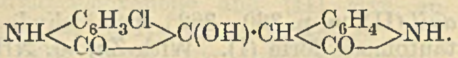
New hypnotic, ethyl-β-ethylbutylbarbituric acid and some derivatives of β-ethylbutyl alcohol. E. Fourneau and J. Matti.—See this vol., 142.

Influence of nitration and amination on the physical and physiological properties of phenylmethylmalonylcarbamide (rutonal) and of phenylethylmalonylcarbamide (gardinal or luminal). A. Leulier and F. Postic (Compt. rend., 1931, **193**, 1476—1478).—Nitro-, m. p. 278°, and amino-phenylethyl-, m. p. 213°, *nitro*-, m. p. 218°, and aminophenylmethyl-malonylcarbamide, m. p. 226°, have lower partition coeffs. between H_2O and olive oil than the unsubstituted compounds, and have no hypnotic action. F. R. Shaw.

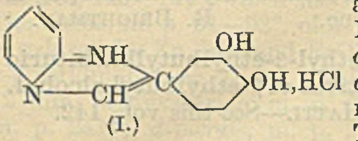
Pyrazole series. Diazotisation of aminophenylpyrazoles. J. Reilly, B. Daly, and P. J. Drumm (Proc. Roy. Irish Acad., 1931, **40**, **B**, 94—101).—Benzoylacetone and *p*-nitrophenylhydrazine give 5-*phenyl*-1-p-*nitrophenyl*-3-*methylpyrazole*, m. p. 100—101°, reduced to the NH_2-derivative, m. p. 150° [*dihydrochloride*, m. p. 245° (decomp.); *Bz* derivative, m. p. 170°; *benzylidene* derivative, m. p. 145°; *chloroplatinate*; *chloroaurate*], which gives a *diazonium chloride* (*chloroplatinate*; *chloroaurate*; *dichromate hydrochloride*). This by coupling with suitable substances gives β-*naphtholazo*-, m. p. 177°, β-*naphthylaminoazo*-, m. p. 182°, *chromotropic acid azo*-, *carbethoxyacetoneazo*-, and *acetylacetoneazo-diphenylmethylpyrazole*, m. p. 159°. The stability of the above diazonium chloride was measured. A. A. Levi.

Constitution of Fischer and Bulow's pyrazole. P. J. Drumm (Proc. Roy. Irish Acad., 1931, **40**, **B**, 106—108).—Condensation of benzoylacetone with $NHPh{\cdot}NH_2$ (A., 1885, 1237) gives a pyrazole, m. p. 63°, purified through the *picrate*, m. p. 124°, and shown to be identical with 1 : 5-diphenyl-3-methylpyrazole (A., 1926, 624). It is converted by MeI into 1 : 5-*diphenyl*-3-*methylpyrazolemethylammonium iodide*, m. p. 186°, and by Br in $CHCl_3$ into 4-bromo-1 : 5-diphenyl-3-methylpyrazole, m. p. 76°, identical with the product of bromination of the diphenylmethylpyrazole obtained from benzoylacetoacetate and $NHPh{\cdot}NH_2$ (A., 1885, 555). A. A. Levi.

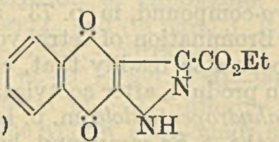
Condensation of chloroisatins with dioxindole and oxindole. G. Fericean (Bull. Soc. Chim. România, 1931, **13**, 27—31).—5- and 7-Chloroisatin condense with dioxindole in the presence of piperidine to give, respectively, 5-, m. p. 255°, and 7-, m. p. 238°, -*chloroisatide*, similar condensation with oxindole giving 5-, m. p. 207°, and 7-, m. p. 182° (decomp.),

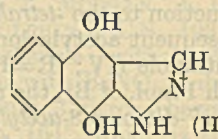
-*chloroisatan*,  $NH<\begin{smallmatrix}C_6H_3Cl\\CO\end{smallmatrix}>C(OH)\cdot CH<\begin{smallmatrix}C_6H_4\\CO\end{smallmatrix}>NH$. When condensation with oxindole is effected in the presence of AcOH–HCl the products are, respectively, 5- [reduced by Zn and AcOH to the leuco-*compound*, m. p. 251° (decomp.)] and 7- (leuco-*compound*), -*chloroisoindigotin*. J. W. Baker.

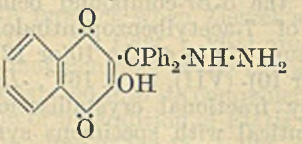
2-3′: 4′-Dihydroxyphenylpyrimidazole. A. E. Tschitschibabin and M. Plaschenkova (Ber., 1931, **64**, [*B*], 2842—2844).—2-Aminopyridine and chloroacetopyrocatechol at 120° yield 2-3′ : 4′-*dihydroxyphenylpyrimidazole hydrochloride* (I), not molten below 285°. The *base*, m. p. 255° (decomp.), and its *picrate*, m. p. 137° (decomp.) (also +EtOH), are described. H. Wren.

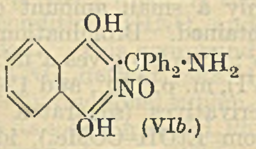

(I.)

Comparison of heterocyclic systems with benzene. III. Addition of diazomethane and its derivatives to α-naphthaquinone. L. F. Fieser and M. A. Peters (J. Amer. Chem. Soc., 1931, **53**, 4080—4093; cf. A., 1927, 1198).—α-Naphthaquinone and $N_2CH\cdot CO_2Et$ in C_6H_6–Et_2O give 48% of α-naphthahydroquinone and 47% of 3-*carbethoxy-lin.-naphthindazole*-4 : 9-*quinone* (I), m. p. 186·5°, which forms a red vat with $Na_2S_2O_4$. The reaction apparently consists in the slow addition of $N_2CH\cdot CO_2Et$ to the quinone, isomerisation of an azo- to a pyrazole ring, enolisation, and subsequent oxidation of the dienol by unreacted quinone. Reductive acetylation of (I) gives the *quinol triacetate*, m. p. 179°. Hydrolysis of (I) gives the free *acid*, m. p. 281°; the vat is red. Diazomethane gives 93% of lin.-*naphthindazole*-4 : 9-*hydroquinone* (II), which changes on crystallisation to *lin.*-naphthindazole-4 : 9-quinone, m. p. 349° (block) (cf. von Pechmann and Seel, A., 1899, i, 947); analysis indicates the formula $C_{11}H_6O_2N_2$, instead of $C_{11}H_8O_2N_2$ (cf. *loc. cit.*). The quinone also results when the above acid is heated at 281° with a trace of Cu powder. The quinone and Me_2SO_4 give the 1-*Me* derivative, m. p. 312°. Diazodiphenylmethane and α-naphthaquinone react vigorously, giving 44% of 2 : 3-(3 : 3-*diphenyl-ψ-pyrazolo*-4 : 5)-1 : 4-*naphthahydroquinone* (III), m. p. 203° [*diacetate*, m. p. 259° (slow decomp.); *monobenzoate* (+H_2O), decomp. about 144°; *dibenzoate*, m. p. 215° (decomp.); *Me*$_2$ *ether*, m. p. 192° (decomp.)]. Oxidation of (III) with HgO in C_6H_6 or with $NaNO_2$ in AcOH gives 2 : 3-(3 : 3-*diphenyl-ψ-pyrazolo*-4 : 5)-1 : 4-*naphthaquinone* (IV), m. p. 231°, whilst reduction with Zn and AcOH gives 3-*amino*-1 : 4-*dihydroxy*-2-(α-*amino*-αα-*diphenylmethylnaphthalene*, m. p. 255° (decomp.) [*diacetate*, m. p. 142° (decomp.)]. Alkaline oxidation of (III) gives 3-hydroxy-2-benzhydryl-1 : 4-naphthaquinone, m. p. 188°. Thermal decomp. of (III) at 205—210° for 5—10 min. gives (IV), 2-benzhydryl-1 : 4-naphthaquinone, (V), m. p. 189°, and 1-*hydroxy*-4-*keto*-2 : 3-(*diphenylmethylene*)-3 : 4-*dihydronaphthalene*, m. p. 274° (*acetate*, m. p. 245°) [reduced to (V)]. Hydrolysis of the diacetate of (III) gives the *compound* (VI*a* or VI*b*), orange (unstable) and red (stable) forms, m. p. 268—269° (decomp.), converted by and Ac_2O into the original diacetate. *p*-Benzoquinone and diazodiphenylmethane give 93% of 2 : 3-(3 : 3-*diphenyl-ψ-pyrazolo*-4 : 5)-*hydroquinone*, m. p. 210° (decomp.) [*diacetate*, m. p. 181° (decomp.); *monobenzoate*, m. p. 192° (decomp.); *Me*$_2$ *ether*, m. p. 196·5°]. A table of reduction potentials at 25° is given.


(I.)


(II.)


(VI*a*.)


(VI*b*.)

C. J. West (*b*).

Reduction of ethyl oximinoacetoacetate. V. Cerchez and (Mlle.) C. Colesiu (Bull. Soc. chim., 1931, [iv], **49**, 1291—1295).—Reduction (Al–Hg; Et_2O) of Et oximinoacetoacetate affords 35% of Et 3 : 6-dimethylpyrazine-2 : 5-dicarboxylate, m. p. 86°, *via* the aminoacetoacetate; in presence of Et acetoacetate, Et dimethylpyrroledicarboxylate, m. p. 134—135°, is obtained. Reduction with Zn in HCO_2H gave 25% of dimethylpyrazinedicarboxylate and not the expected formylaminoacetoacetate. R. Brightman.

Synthesis of 3-keto-1-ethyl-1 : 2 : 3 : 4-tetrahydroquinoxaline. P. van Romburgh and W. B. Deys (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 1004—1006).—The constitution of 6-nitro-3-keto-1-ethyl-1 : 2 : 3 : 4-tetrahydroquinoxaline (A., 1928, 428) is confirmed by reduction with Fe and HCl, and subsequent elimination of the NH_2-group by diazotisation in EtOH and heating, which gives 3-*keto*-1-*ethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 98—99°, identical with the product obtained from EtI and 3-ketotetrahydroquinoxaline (cf. A., 1886, 351). *Me phenylethylaminoacetate*, b. p. 145—146°/18 mm., prepared from $CH_2Cl\cdot CO_2Me$ and NHPhEt at 130°, is converted by HNO_3 (*d* 1·4) in AcOH into the 2 : 4-(*NO*$_2$)$_2$-derivative, m. p. 119° (identified by oxidation by CrO_3 in aq. AcOH to 2 : 4-dinitroaniline); attempted partial reduction of this with NH_4SH gave indefinite products. H. A. Piggott.

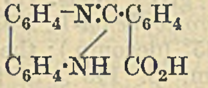
Coloured salts of the dipyridyl series. Theory of quinhydrones. E. Weitz and E. Meitzner (Ber., 1931, **64**, [*B*], 2909—2913).—In analogy with the quinhydrones, the colour of onium salts is attributed to the incomplete heteropolarity of their components. The cyclic, unsaturated onium radicals are shown by the readiness of their chemical or electrochemical reduction to be comparatively "noble," much more so than the alkali-like, tetra-alkylammonium radicals. The intensity of the colour of onium salts increases in solution in the order H_2O, EtOH, $COMe_2$, $CHCl_3$, and this sequence is maintained for the influence of solvent on the oxidisability of the dipyridinium radicals and the decomp. tension of their salts. The effect of the electro-affinity of the anion radical is shown in the following series of 1 : 1′-dibenzyl-4 : 4′-dipyridinium salts, generally prepared by double decomp. from the chloride: *dithiocyanate*, decomp.

about 180°, orange-yellow; *diselenocyanide*, dark red; *thiosulphate*, anhyd. black, *tetrahydrate*, red; unstable *dinitrite*, pale yellow; *diazide*, yellow; *sulphite*, orange-red; *cyanide* and normal *sulphite* are yellow in H_2O; *fluoride*, *cyanide*, *acetate*, and *oxalate* are colourless; *picrate* and *chromate* are yellow, corresponding with the colour proper to the anion. Complete parallelism exists between the depth of colour of the salts and the "nobility" of the anion radical according to Birckenbach and Kellermann. Towards solvents, the salts show the same behaviour as the known onium salts, being darker in org. media, paler in H_2O, or colourless if the solution is sufficiently dil.

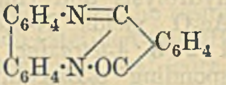
H. WREN.

Condensation products of anhydrides of dibasic acids with aromatic diamines. L. GUGLIALMELLI, P. CHANUSSOT, and C. L. RUÍZ (Anal. Asoc. Quím. Argentina, 1930, 18, 257—273).—The interaction of phthalic anhydride with benzidine is considered to be analogous to that with *o*-phenylenediamine. Condensation in H_2O at 100°, or in cold C_6H_6, treatment of the product with warm 1% NaOH, and acidification yields a *substance* regarded as (I), m. p. indef., which loses $1H_2O$ at 120°/10 mm. to give (II), m. p. 309°. Amine reactions with (II) were obtained only under conditions in which decomp. occurs. It could be diazotised only in 50% HCl, and addition of H_2O to the solution in H_2SO_4 yielded a diazotisable sulphate of monophthalylbenzidine, which is converted by NaOH into the Na salt of (I), or by $NaCO_3$ into (II). Benzylidenemonophthalylbenzidine (A., 1926, 1131) has m. p. 333°.

(I.)



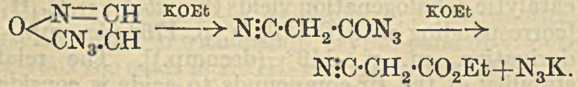
(II.)



R. K. CALLOW.

Action of nitric acid on acetylene. VI. A. QUILICO (Gazzetta, 1931, 61, 759—772).—The compound $C_3H_2ON_4$ (cf. A., 1931, 1169) condenses with C_2H_2, giving a *triazole*, m. p. 126°, and with CH:CPh, giving a C-*phenyltriazole*, m. p. 154°, showing that it is a diazoimide, $(C_3H_2ON)N_3$ (I). With KOH–EtOH (I) gives N_3H and a dibasic *acid*, $(C_5H_4ON_5)CO_2H$ (II), m. p. 163—165° (decomp.) [*Ac* derivative, m. p. 205° (decomp.) $+2H_2O$; $+0{\cdot}5H_2O$; *Ag* salt], giving with diazomethane a *Me₂* derivative, m. p. 120°, $Me(C_5H_3ON_5)CO_2Me$, converted by KOH into the *Me* derivative, $Me(C_5H_3ON_5){\cdot}CO_2H$, m. p. 190° (decomp.). Adopting the α-*iso*oxazolediazoimide formula for (I) the reaction is explained thus:

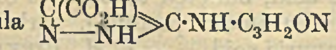
(*a*)



$$O\genfrac{<}{}{0pt}{}{N{=}CH}{CN_3{:}CH} \xrightarrow{\text{KOEt}} N{:}C{\cdot}CH_2{\cdot}CON_3 \xrightarrow{\text{KOEt}} N{:}C{\cdot}CH_2{\cdot}CO_2Et + N_3K.$$

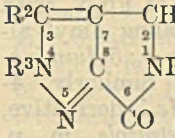
(*b*) $$N{:}C{\cdot}CH_2{\cdot}CO_2Et + C_3H_2ON_4 \longrightarrow (C_5H_4ON_5){\cdot}CO_2Et \quad \text{(III.)}$$

This is confirmed by the fact that Et cyanoacetate condenses with (I), giving the Et ester (III), m. p. 230° (decomp.) (*Ac* derivative, m. p. 148°), of (II), for which the formula $\genfrac{}{}{0pt}{}{C(CO_2H)}{N{-}{-}NH}{>}C{\cdot}NH{\cdot}C_3H_2ON$ is suggested. The compounds $C_3H_5ON_3$ and $C_3H_4ON_2$ are probably α-*iso*oxazolylhydrazine and α-*iso*oxazolylamine.



E. E. J. MARLER.

Pyrazopyrrolidones. M. DOHRN and A. THIELE (Ber., 1931, 64, [*B*], 2863—2865).—Acetylpyruvic ester, PhCHO and NH_3, in C_6H_6–EtOH give 4 : 5-*diketo-3-acetyl-2-phenylpyrrolidine*, m. p. 195—196°, the *phenylhydrazone*, m. p. 217°, of which passes in boiling EtOH containing H_2SO_4 into 2 : 4-*diphenyl-3-methylpyrazopyrrolid-6-one*, m. p. 214—215° (cf. I). The following substances are similarly derived: 4 : 5-*diketo-3-acetyl-2-phenyl-1-methylpyrrolidine*, m. p. 215—216° after softening (from acetylpyruvic ester, NH_2Me and PhCHO), its *methylhydrazone*, m. p. 204—205°, and 2-*phenyl*-1 : 3 : 4-*trimethylpyrazopyrrolid-6-one*, m. p. 250—255° after softening; 4 : 5-*diketo-3-acetyl-2-piperonylpyrrolidine*, m. p. 158—159°, its phenylhydrazone and 4-*phenyl-2-piperonyl-3-methylpyrazopyrrolid-6-one*, m. p. 216—217°; 4 : 5-diketo-3-acetyl-1 : 2-diphenylpyrrolidine, m. p. 229—231° (decomp.), its phenylhydrazone and 1 : 2 : 4-*triphenyl-3-methylpyrazopyrrolid-6-one*, m. p. 174—175°; 4 : 5-*diketo-3-acetyl*-1 : 2-*diphenylpyrrolidine*-p-*tolylhydrazone*, m. p. 218° (decomp.), and 1 : 2-*diphenyl*-4-p-*tolyl-3-methylpyrazopyrrolid-6-one*, m. p. 158—159°; 4 : 5-diketo-3-acetyl-1-*m*-tolyl-2-*p*-methoxyphenylpyrrolidine, m. p. 186—188° (from *m*-toluidine, anisaldehyde, and Et acetylpyruvate in C_6H_6), its phenylhydrazone and 4-*phenyl*-1-m-*tolyl*-2-p-*methoxyphenyl-3-methylpyrazopyrrolid-6-one*, m. p. 167—169°; 4 : 5-*diketo-3-acetyl*-1-o-*methoxyphenyl*-2-p-*methoxyphenylpyrrolidine*, m. p. 218—220° after darkening at 210°, its phenylhydrazone and 4-*phenyl*-1-o-*methoxyphenyl*-2-p-*methoxyphenyl-3-methylpyrazopyrrolid-6-one*, m. p. 161—163°; 4 : 5-*diketo-3-acetyl*-1 : 2-*di*-p-*methoxyphenylpyrrolidine*, m. p. 163—164°, its phenylhydrazone and 4-*phenyl*-1 : 2-*di*-p-*methoxyphenyl-3-methylpyrazopyrrolid-6-one*, m. p. 162—164°: 1 : 2 : 3 : 4-*tetraphenylpyrazopyrrolid-6-one*, m. p. 195—197°.

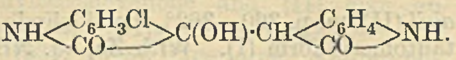


(I.)

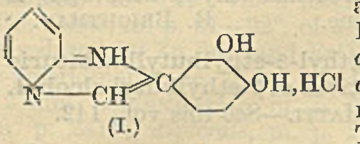
H. WREN.

Optically active *spiro*-5 : 5-dihydantoins. (SIR) W. J. POPE and J. B. WHITWORTH (Proc. Roy. Soc., 1931, A, 134, 357—371).—When *dl-spiro*-5 : 5-dihydantoin [Ac_2 derivative (modified prep.), $+H_2O$, m. p. 248—249°; 1 : 9-Bz_2 derivative, m. p. 295° (decomp.) after darkening at 290°] (1 mol.) is boiled with brucine (2 mols.) in EtOH and cooled, the *brucine* salt, $+H_2O$ (lost at 125—135° in vac.), m. p. 259—260°, of l-spiro-5 : 5-*dihydantoin*, $+H_2O$, darkens at 240°, m. p. above 320° [1 : 9-*Ac₂* derivative, m. p. 262—264°; 1 : 9-*Bz₂*-derivative, m. p. 307—308° (decomp.) after darkening at 280°], separates; when the mother-liquor is kept, the *dibrucine* salt, $+2H_2O$ (1·5 mols. lost at 120—130° in vac.), m. p. 205—206° (decomp.), of the d-*isomeride* crystallises. The rotatory dispersions of the *d*-base in EtOH, pyridine, H_2O, and 1, 2, and 4 mols. of aq. NaOH indicate the existence of the substance in diketonic, mono- and di-enolic forms. Optical data, crystal form, and *X*-ray structure are recorded for the *dl*- and *l*-forms. The crystal of the *dl*-base contains alternate layers of *d*- and *l*-mols., has a higher *d*, and is more closely packed than that of the active forms; the high *d* is possibly connected with the high m. p. and low solubility.

R. S. CAHN.

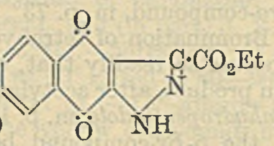
-chloroisatan,  $NH{<}\substack{C_6H_3Cl \\ CO-}{>}C(OH){\cdot}CH{<}\substack{C_6H_4 \\ CO-}{>}NH$. When condensation with oxindole is effected in the presence of AcOH–HCl the products are, respectively, 5- [reduced by Zn and AcOH to the leuco-*compound*, m. p. 251° (decomp.)] and 7- (leuco-*compound*), *-chloroisoindigotin.* J. W. Baker.

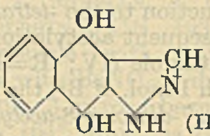
2-3′ : 4′-Dihydroxyphenylpyrimidazole. A. E. Tschitschibabin and M. Plaschenkova (Ber., 1931, 64, [*B*], 2842—2844).—2-Aminopyridine and chloroacetopyrocatechol at 120° yield 2-3′ : 4′-*dihydroxyphenylpyrimidazole hydrochloride* (I), not molten below 285°. The *base*, m. p. 255° (decomp.), and its *picrate*, m. p. 137° (decomp.) (also +EtOH), are described. H. Wren.



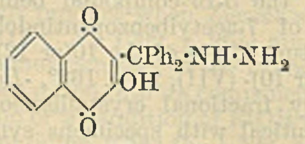
(I.)

Comparison of heterocyclic systems with benzene. III. Addition of diazomethane and its derivatives to α-naphthaquinone. L. F. Fieser and M. A. Peters (J. Amer. Chem. Soc., 1931, 53, 4080—4093; cf. A., 1927, 1198).—α-Naphthaquinone and $N_2CH{\cdot}CO_2Et$ in C_6H_6–Et_2O give 48% of α-naphthahydroquinone and 47% of 3-*carbethoxy*-lin.-*naphthindazole*-4 : 9-*quinone* (I), m. p. 186·5°, which forms a red vat with $Na_2S_2O_4$. The reaction apparently consists in the slow addition of $N_2CH{\cdot}CO_2Et$ to the quinone, isomerisation of an azo- to a pyrazole ring, enolisation, and subsequent oxidation of the dienol by unreacted quinone. Reductive acetylation of (I) gives the *quinol triacetate*, m. p. 179°. Hydrolysis of (I) gives the free *acid*, m. p. 281°; the vat is red. Diazomethane gives 93% of lin.-*naphthindazole*-4 : 9-*hydroquinone* (II), which changes on crystallisation to *lin.*-naphthindazole-4 : 9-quinone, m. p. 349° (block) (cf. von Pechmann and Seel, A., 1899, i, 947); analysis indicates the formula $C_{11}H_6O_2N_2$, instead of $C_{11}H_8O_2N_2$ (cf. *loc. cit.*). The quinone also results when the above acid is heated at 281° with a trace of Cu powder. The quinone and Me_2SO_4 give the 1-*Me* derivative, m. p. 312°. Diazodiphenylmethane and α-naphthaquinone react vigorously, giving 44% of 2 : 3-(3 : 3-*diphenyl*-ψ-*pyrazolo*-4 : 5)-1 : 4-*naphthahydroquinone* (III), m. p. 203° [*diacetate*, m. p. 259° (slow decomp.); *monobenzoate* (+H_2O), decomp. about 144°; *dibenzoate*, m. p. 215° (decomp.); *Me_2 ether*, m. p. 192° (decomp.)]. Oxidation of (III) with HgO in C_6H_6 or with $NaNO_2$ in AcOH gives 2 : 3-(3 : 3-*diphenyl*-ψ-*pyrazolo*-4 : 5)-1 : 4-*naphthaquinone* (IV), m. p. 231°, whilst reduction with Zn and AcOH gives 3-*amino*-1 : 4-*dihydroxy*-2-(α-*amino*-αα-*diphenylmethylnaphthalene*, m. p. 255° (decomp.) [*diacetate*, m. p. 142° (decomp.)]. Alkaline oxidation of (III) gives 3-hydroxy-2-benzhydryl-1 : 4-naphthaquinone, m. p. 188°. Thermal decomp. of (III) at 205—210° for 5—10 min. gives (IV), 2-benzhydryl-1 : 4-naphthaquinone, (V), m. p. 189°, and 1-*hydroxy*-4-*keto*-2 : 3-(*diphenylmethylene*)-3 : 4-*dihydronaphthalene*, m. p. 274° (*acetate*, m. p. 245°) [reduced to (V)]. Hydrolysis of the diacetate of (III) gives the *compound* (VI*a* or VI*b*), orange (unstable) and red (stable) forms, m. p. 268—269° (decomp.), converted by and Ac_2O into the original diacetate. *p*-Benzoquinone and diazodiphenylmethane give 93% of 2 : 3-(3 : 3-*diphenyl*-ψ-*pyrazolo*-4 : 5)-*hydroquinone*, m. p. 210° (decomp.) [*diacetate*, m. p. 181° (decomp.); *monobenzoate*, m. p. 192° (decomp.); *Me_2 ether*, m. p. 196·5°]. A table of reduction potentials at 25° is given.

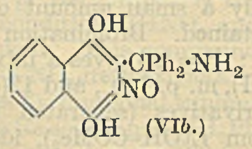
(I.)




(II.)



(VI*a*.)



(VI*b*.)

C. J. West (*b*).

Reduction of ethyl oximinoacetoacetate. V. Cerchez and (Mlle.) C. Colesiu (Bull. Soc. chim., 1931, [iv], 49, 1291—1295).—Reduction (Al–Hg; Et_2O) of Et oximinoacetoacetate affords 35% of Et_2 3 : 6-dimethylpyrazine-2 : 5-dicarboxylate, m. p. 86°, *via* the aminoacetoacetate; in presence of Et acetoacetate, Et dimethylpyrroledicarboxylate, m. p. 134—135°, is obtained. Reduction with Zn in HCO_2H gave 25% of dimethylpyrazinedicarboxylate and not the expected formylaminoacetoacetate, R. Brightman.

Synthesis of 3-keto-1-ethyl-1 : 2 : 3 : 4-tetrahydroquinoxaline. P. van Romburgh and W. B. Deys (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1004—1006).—The constitution of 6-nitro-3-keto-1-ethyl-1 : 2 : 3 : 4-tetrahydroquinoxaline (A., 1928, 428) is confirmed by reduction with Fe and HCl, and subsequent elimination of the NH_2-group by diazotisation in EtOH and heating, which gives 3-*keto*-1-*ethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 98—99°, identical with the product obtained from EtI and 3-ketotetrahydroquinoxaline (cf. A., 1886, 351). *Me phenylethylaminoacetate*, b. p. 145—146°/18 mm., prepared from $CH_2Cl{\cdot}CO_2Me$ and NHPhEt at 130°, is converted by HNO_3 (*d* 1·4) in AcOH into the 2 : 4-$(NO_2)_2$-derivative, m. p. 119° (identified by oxidation by CrO_3 in aq. AcOH to 2 : 4-dinitroaniline); attempted partial reduction of this with NH_4SH gave indefinite products. H. A. Piggott.

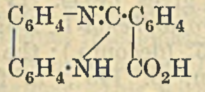
Coloured salts of the dipyridyl series. Theory of quinhydrones. E. Weitz and E. Meitzner (Ber., 1931, 64, [*B*], 2909—2913).—In analogy with the quinhydrones, the colour of onium salts is attributed to the incomplete heteropolarity of their components. The cyclic, unsaturated onium radicals are shown by the readiness of their chemical or electrochemical reduction to be comparatively " noble," much more so than the alkali-like, tetra-alkylammonium radicals. The intensity of the colour of onium salts increases in solution in the order H_2O, EtOH, $COMe_2$, $CHCl_3$, and this sequence is maintained for the influence of solvent on the oxidisability of the dipyridinium radicals and the decomp. tension of their salts. The effect of the electro-affinity of the anion radical is shown in the following series of 1 : 1′-dibenzyl-4 : 4′-dipyridinium salts, generally prepared by double decomp. from the chloride: *dithiocyanate*, decomp.

about 180°, orange-yellow; *diselenocyanide*, dark red; *thiosulphate*, anhyd. black, *tetrahydrate*, red; unstable *dinitrite*, pale yellow; *diazide*, yellow; *sulphite*, orange-red; *cyanide* and normal *sulphite* are yellow in H_2O; *fluoride*, *cyanide*, *acetate*, and *oxalate* are colourless; *picrate* and *chromate* are yellow, corresponding with the colour proper to the anion. Complete parallelism exists between the depth of colour of the salts and the "nobility" of the anion radical according to Birckenbach and Kellermann. Towards solvents, the salts show the same behaviour as the known onium salts, being darker in org. media, paler in H_2O, or colourless if the solution is sufficiently dil.

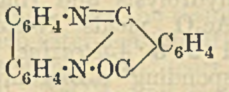
H. Wren.

Condensation products of anhydrides of dibasic acids with aromatic diamines. L. Guglialmelli, P. Chanussot, and C. L. Ruíz (Anal. Asoc. Quím. Argentina, 1930, **18**, 257—273).—The interaction of phthalic anhydride with benzidine is considered to be analogous to that with *o*-phenylenediamine. Condensation in H_2O at 100°, or in cold C_6H_6, treatment of the product with warm 1% NaOH, and acidification yields a *substance* regarded as (I), m. p. indef., which loses $1H_2O$ at 120°/10 mm. to give (II), m. p. 309°. Amine reactions with (II) were

(I.)



(II.)

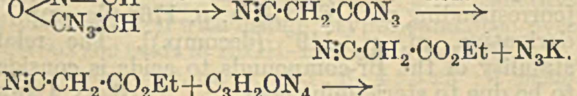


obtained only under conditions in which decomp. occurs. It could be diazotised only in 50% HCl, and addition of H_2O to the solution in H_2SO_4 yielded a diazotisable sulphate of monophthalylbenzidine, which is converted by NaOH into the Na salt of (I), or by $NaCO_3$ into (II). Benzylidenemonophthalylbenzidine (A., 1926, 1131) has m. p. 333°.

R. K. Callow.

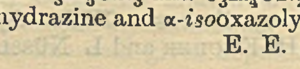
Action of nitric acid on acetylene. VI. A. Quilico (Gazzetta, 1931, **61**, 759—772).—The compound $C_3H_2ON_4$ (cf. A., 1931, 1169) condenses with C_2H_2, giving a *triazole*, m. p. 126°, and with CH⋮CPh, giving a C-*phenyltriazole*, m. p. 154°, showing that it is a diazoimide, $(C_3H_2ON)N_3$ (I). With KOH–EtOH (I) gives N_3H and a dibasic *acid*, $(C_5H_4ON_5)CO_2H$ (II), m. p. 163—165° (decomp.) [*Ac* derivative, m. p. 205° (decomp.) $+2H_2O$; $+0{\cdot}5H_2O$; *Ag* salt], giving with diazomethane a *Me*₂ derivative, m. p. 120°, $Me(C_5H_3ON_5)CO_2Me$, converted by KOH into the *Me* derivative, $Me(C_5H_3ON_5){\cdot}CO_2H$, m. p. 190° (decomp.). Adopting the α-*iso*oxazolediazoimide formula for (I) the reaction is explained thus:

(*a*)



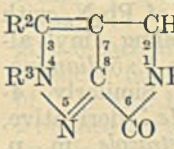
$$O{<}\begin{matrix}N{=}CH\\ CN_3{:}CH\end{matrix}\xrightarrow{KOEt}N{⋮}C{\cdot}CH_2{\cdot}CON_3\xrightarrow{KOEt}N{⋮}C{\cdot}CH_2{\cdot}CO_2Et+N_3K.$$

(*b*) $N{⋮}C{\cdot}CH_2{\cdot}CO_2Et+C_3H_2ON_4\longrightarrow(C_5H_4ON_5){\cdot}CO_2Et$ (III.)

This is confirmed by the fact that Et cyanoacetate condenses with (I), giving the Et ester (III), m. p. 230° (decomp.) (*Ac* derivative, m. p. 148°), of (II), for which the formula  $\begin{matrix}C(CO_2H)\\ N{-}NH\end{matrix}{>}C{\cdot}NH{\cdot}C_3H_2ON$ is suggested. The compounds $C_3H_5ON_3$ and $C_3H_4ON_2$ are probably α-*iso*oxazolylhydrazine and α-*iso*oxazolylamine.

E. E. J. Marler.

Pyrazopyrrolidones. M. Dohrn and A. Thiele (Ber., 1931, **64**, [*B*], 2863—2865).—Acetylpyruvic ester, PhCHO and NH_3, in C_6H_6–EtOH give 4:5-*diketo*-3-*acetyl*-2-*phenylpyrrolidine*, m. p. 195—196°, the *phenylhydrazone*, m. p. 217°, of which passes in boiling EtOH containing H_2SO_4 into 2:4-*diphenyl*-3-*methylpyrazopyrrolid*-6-*one*, m. p. 214—215° (cf. I).



(I.)

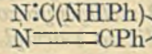
The following substances are similarly derived: 4:5-*diketo*-3-*acetyl*-2-*phenyl*-1-*methylpyrrolidine*, m. p. 215—216° after softening (from acetylpyruvic ester, NH_2Me and PhCHO), its *methylhydrazone*, m. p. 204—205°, and 2-*phenyl*-1:3:4-*trimethylpyrazopyrrolid*-6-*one*, m. p. 250—255° after softening; 4:5-*diketo*-3-*acetyl*-2-*piperonylpyrrolidine*, m. p. 158—159°, its phenylhydrazone and 4-*phenyl*-2-*piperonyl*-3-*methylpyrazopyrrolid*-6-*one*, m. p. 216—217°; 4:5-diketo-3-acetyl-1:2-diphenylpyrrolidine, m. p. 229—231° (decomp.), its phenylhydrazone and 1:2:4-*triphenyl*-3-*methylpyrazopyrrolid*-6-*one*, m. p. 174—175°; 4:5-*diketo*-3-*acetyl*-1:2-*diphenylpyrrolidine*-p-*tolylhydrazone*, m. p. 218° (decomp.), and 1:2-*diphenyl*-4-p-*tolyl*-3-*methylpyrazopyrrolid*-6-*one*, m. p. 158—159°; 4:5-diketo-3-acetyl-1-*m*-tolyl-2-*p*-methoxyphenylpyrrolidine, m. p. 186—188° (from *m*-toluidine, anisaldehyde, and Et acetylpyruvate in C_6H_6), its phenylhydrazone and 4-*phenyl*-1-m-*tolyl*-2-p-*methoxyphenyl*-3-*methylpyrazopyrrolid*-6-*one*, m. p. 167—169°; 4:5-*diketo*-3-*acetyl*-1-o-*methoxyphenyl*-2-p-*methoxyphenylpyrrolidine*, m. p. 218—220° after darkening at 210°, its phenylhydrazone and 4-*phenyl*-1-o-*methoxyphenyl*-2-p-*methoxyphenyl*-3-*methylpyrazopyrrolid*-6-*one*, m. p. 161—163°; 4:5-*diketo*-3-*acetyl*-1:2-*di*-p-*methoxyphenylpyrrolidine*, m. p. 163—164°, its phenylhydrazone and 4-*phenyl*-1:2-*di*-p-*methoxyphenyl*-3-*methylpyrazopyrrolid*-6-*one*, m. p. 162—164°: 1:2:3:4-*tetraphenylpyrazopyrrolid*-6-*one*, m. p. 195—197°.

H. Wren.

Optically active *spiro*-5:5-dihydantoins. (Sir) W. J. Pope and J. B. Whitworth (Proc. Roy. Soc., 1931, **A**, **134**, 357—371).—When *dl*-*spiro*-5:5-dihydantoin [Ac_2 derivative (modified prep.), $+H_2O$, m. p. 248—249°; 1:9-Bz_2 derivative, m. p. 295° (decomp.) after darkening at 290°] (1 mol.) is boiled with brucine (2 mols.) in EtOH and cooled, the *brucine* salt, $+H_2O$ (lost at 125—135° in vac.), m. p. 259—260°, of l-spiro-5:5-*dihydantoin*, $+H_2O$, darkens at 240°, m. p. above 320° [1:9-Ac_2 derivative, m. p. 262—264°; 1:9-Bz_2-derivative, m. p. 307—308° (decomp.) after darkening at 280°], separates; when the mother-liquor is kept, the *dibrucine* salt, $+2H_2O$ (1·5 mols. lost at 120—130° in vac.), m. p. 205—206° (decomp.), of the d-*isomeride* crystallises. The rotatory dispersions of the *d*-base in EtOH, pyridine, H_2O, and 1, 2, and 4 mols. of aq. NaOH indicate the existence of the substance in diketonic, mono- and di-enolic forms. Optical data, crystal form, and *X*-ray structure are recorded for the *dl*- and *l*-forms. The crystal of the *dl*-base contains alternate layers of *d*- and *l*-mols., has a higher *d*, and is more closely packed than that of the active forms; the high *d* is possibly connected with the high m. p. and low solubility.

R. S. Cahn.

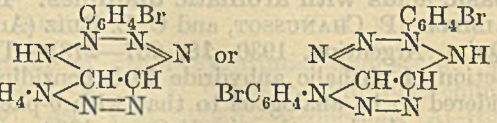
1 : 5-Diamino- and 1-amino-5-hydrazino-tetrazoles. R. STOLLÉ and E. GAERTNER (J. pr. Chem., 1931, [ii], **132**, 209—226).—Interaction of thiosemicarbazide with PbO and NaN_3 in boiling EtOH in a stream of CO_2, followed by acidification with aq. HCl and shaking with PhCHO, gives 1-*benzylideneamino*-5-*aminotetrazole*, m. p. 210° (decomp.), also obtained in poor yield by interaction of Pb_2N_6 with benzaldehydethiosemicarbazone in boiling amyl alcohol; hydrolysis with 10% HCl gives 1 : 5-*diaminotetrazole hydrochloride*, m. p. 176°. Similarly, 4-phenylthiosemicarbazide and its CMe_2**:** derivative, m. p. 130°, give 1-*amino*-5-*anilinotetrazole*, m. p. 210° (decomp.) [1-N-CMe_2**:** derivative, m. p. 136° (action of $COMe_2$ at 100°)], but benzaldehyde-4-phenylthiosemicarbazone gives the *CHPh***:** derivative, m. p. 216°. The first method gives as by-product 3 : 6-*dianilino*-1 : 2-*dihydro*-1 : 2 : 4 : 5-*tetrazine*, m. p. 275° (decomp.) [*hydrochloride*, m. p. 172° (decomp., sinters at 150°)], also obtained by action of PbO alone on 4-phenylthiosemicarbazide. 1-*Benzylideneamino*-5-*allylamino*-, m. p. 117°, and 1-*amino*-5-*allylamino-tetrazole*, m. p. 94°, are similarly prepared, the latter being accompanied by 3 : 6-*diallylamino*-1 : 2 : 4 : 5-*tetrazine*, m. p. 118°.

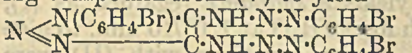
Thiocarbohydrazide (prep. improved) with NaN_3 and PbO gives 1-amino-5-hydrazinotetrazole [*hydrochloride*, m. p. 171° (decomp.); $(CHPh:)_2$ derivative, m. p. 225° (decomp.)]; this appears to be converted by diazotisation into Thiele's tetrazyl azide (A., 1896, i, 107). From 1-benzoyl-4-phenylthiosemicarbazide is obtained, not the tetrazole, but 2-*anilino*-5-*phenyl*-1 : 3 : 4-*furodiazole*,  $\left.\begin{matrix}N{:}C(NHPh)\\ N{=\!=\!=}CPh\end{matrix}\right>O$, m. p. 217° ($+xAgNO_3$, decomp. 200°), also obtained by action of PbO, CO_2, and EtOH alone. This is converted by $NaNO_2$ and AcOH into two NO_2-compounds, m. p. 278° and 168°, by N_2O_3 in AcOH into an $(NO_2)_2$-derivative, m. p. 231°, and by HNO_3–H_2SO_4 into a *substance*, m. p. 207°. From hydrazine dithiocarbazinate ($NH_2{\cdot}NH{\cdot}CS{\cdot}S,N_2H_4$) is obtained 1-amino-5-hydrazinotetrazole, carbohydrazide, thiocarbohydrazide (*CHPh***:** derivative, m. p. 193°), and, as its *CHPh* derivative, m. p. 173° (decomp.), the compound $NH_2{\cdot}NH{\cdot}CS{\cdot}N_3$. The yields of tetrazoles obtained in these reactions are considerably reduced if the CO_2 be replaced by H_2. H. A. PIGGOTT.

Reaction between magnesium acetylenyl bromide and azides. H. KLEINFELLER and G. BÖNIG (J. pr. Chem., 1931, [ii], **132**, 175—199).—Mg acetylenyl bromide and PhN_3 give partly $[NPh{:}N{\cdot}N(MgBr){\cdot}C{:}]_2$, which on decomp. affords bisphenyltriazenoacetylene (I), m. p. 174° (A., 1928, 630, m. p. 170°), and partly $[NPh{:}N{\cdot}N{:}C(MgBr){\cdot}]_2$, which affords the *substance* $(NPh{:}N{\cdot}N{:}CH{\cdot})_2$ (II), m. p. 170°, on decomp. The substance, m. p. 156° (*loc. cit.*), is a mixture of (II) and the substance, $C_8H_8N_4$, m. p. 172° (III). The constitutions assigned (*loc. cit.*) to (I) and 2-phenyl-1 : 2-dihydro-1 : 2 : 3 : 4-tetrazine (IV) are confirmed. (I) and boiling AcOH give the N-*Ac* derivative of (IV), m. p. 219°, this and the N-*formyl* derivative (similarly obtained), m. p. 172°, being converted by NaOH in hot EtOH into (IV) (*hydrochloride*, m. p. 185°; *NO*-derivative, explosive, giving with NaOH a violet *additive* compound, $C_8H_8N_5O_2Na$, decomp. 175°; o-*Br*-derivative, m. p. 135°). (II) with cold H_2SO_4 gives (III) [does not form acyl derivatives; *hydrochloride*, hydrolysed by H_2O or EtOH; o-*Br*-derivative, m. p. 150° (decomp.)], considered to be 2-*phenyl*-2 : 5-*dihydro*-1 : 2 : 3 : 4-*tetrazine*.

Mg acetylenyl bromide and *p*-bromophenyl azide give a little *bis*-p-*bromophenyltriazenoacetylene* (V), m. p. 198° (by normal reaction), much 1-p-*bromophenyl*-4-p-*bromophenyltriazeno*-1 : 2 : 3-*triazole* (VI), m. p. 215° [by addition to the half-reaction product $C(MgBr){:}C{\cdot}NH{\cdot}N{:}N{\cdot}C_6H_4Br$] [previously (*loc. cit.*) assigned the constitution now given to (V)], and the *substance* (VII), $C_{14}H_{11}N_7Br_2$, m. p. 203°. The last compound is formed by addition of the azide to the Mg compound from (V) to yield

(VII.)





$$N{\lessgtr}\begin{matrix}N(C_6H_4Br){\cdot}C{\cdot}NH{\cdot}N{:}N{\cdot}C_6H_4Br\\ N{-\!-\!-\!-\!-\!-}C{\cdot}NH{\cdot}N{:}N{\cdot}C_6H_4Br\end{matrix}$$

(VIII), which by hydrolysis and ring-closure gives (VII). (V) with Ac_2O yields N-*acetyl*-2-p-*bromophenyl*-1 : 2-*dihydro*-1 : 2 : 3 : 4-*tetrazine*, m. p. 265° (decomp.); the corresponding o-*Br*-compound, m. p. 148°, is formed by bromination of the Ac derivative of (IV). When shaken in alcoholic KOH with palladised $CaCO_3$ in presence of H_2 at 4 atm., (V) gives (I), whereby its constitution is proved. With conc. acids (VI) [*Ac* derivative, m. p. 172° (decomp.)] forms diacidic salts [*dinitrate*, m. p. 153° (decomp.); (?) *disulphate*, m. p. 143° (decomp.); $4C_{14}H_{10}N_6Br_2,3H_2SO_4$, m. p. 195°], hydrolysed by H_2O to monoacidic salts [*nitrate*, m. p. 174° (decomp.)], from which the former are regenerated by conc. acids. (VII) is unaffected by most reducing agents, but with Zn dust and AcOH gives a *dihydro*-derivative, m. p. 224° (decomp.), and with H_2 at 4 atm. in presence of palladised $CaCO_3$ in alcoholic KOH affords 1-*phenyl*-4-*phenyltriazeno*-1 : 2 : 3-*triazole*, m. p. 108° (*Br*-derivative, m. p. 206°), which with hot dil. HCl gives 4-*amino*-1-*phenyl*-1 : 2 : 3-*triazole*, m. p. 110° [*Br*-derivative, m. p. 172°; *Ac* derivative, m. p. 143° (*Br*-derivative, m. p. 178°)]; the aminotriazole and HNO_2 give N_2 and 4-*hydroxy*-1-*phenyl*-1 : 2 : 3-*triazole*, m. p. 160°. (VII) {*Ac* derivative, m. p. 149° (decomp.); *NO* derivative, m. p. 103° (decomp.) [*nitrate*, m. p. 162°, (decomp.)]} on catalytic dehalogenation yields the *substance*, $C_{14}H_{13}N_7$ [corresponding with (VII)], m. p. 176° (decomp.) [*Ac* derivative, m. p. 149° (decomp.)]. The relative stability of the Br-compounds to acids is considered to be due to steric influences. R. S. CAHN.

Oxidation of uric acid by hydrogen peroxide under physiological conditions. H. WIELAND and T. F. MACRAE (Z. physiol. Chem., 1931, **203**, 83—86).—Uric acid, buffered to p_H 8, is oxidised by H_2O_2 to allantoin (main product), carbonyldicarbamide, and cyanuric acid. J. H. BIRKINSHAW.

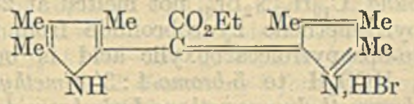
Porphyrin syntheses. XLI. Synthesis of hæmin III. H. FISCHER and L NÜSSLER (Annalen, 1931, 491, 162—188).—2 : 3-Dimethylpyrrole (I), obtained from its 4-carboxylic acid and glycerol at 210°, is converted by the Gattermann method into 2 : 3-*dimethylpyrrole-5-aldehyde* (II), m. p. 126° [*oxime*, m. p. 121°; *semicarbazone*, m. p. 202° (corr.); *azine*, m. p. 180° (corr.)]. (I) and (II) condensed with 48% HBr in EtOH give 4 : 5 : 4′ : 5′-*tetramethylpyrromethene hydrobromide* (III), m. p. 213° (corr.). 5 : 5′-Dibromo-4 : 4′-dimethyl-3 : 3′-di-β-carboxyethylpyrromethene hydrobromide heated with the Br_2-derivative of (III) and succinic acid at 190°, gives, after esterification (MeOH–HCl), 7% of the Me_2 ester, m. p. 290° (corr.) [Br_2-derivative, m. p. 306° (corr.); *Cu* salt, m. p. 288° (corr.); *hæmin*, m. p. 285° (corr.)], of *deuteroporphyrin III* [*hydrochloride*; *hæmin* (IV)]. (IV) and Ac_2O in presence of $SnCl_4$ give, after removal of Fe with HBr in AcOH, *diacetyldeuteroporphyrin III* {Me_2 ester, m. p. 311° (corr.) [*dioxime*; *Cu* salt, m. p. 259° (corr.); *hæmin*, m. p. 298° (corr.)]}, converted by EtOH–KOH into *hæmatoporphyrin III* (30% yield). Prolonged treatment of this with HBr in AcOH, removal of volatile products, dissolution of the residue in MeOH, and subsequent addition of MeOH–KOH gives *tetramethylhæmatoporphyrin III*, decomp. 178° (corr.) with elimination of MeOH. When hæmatoporphyrin III is heated at 125°/high vac., the resulting product fractionated, and then esterified (MeOH–HCl), *protoporphyrin III* Me_2 ester, m. p. 284° (corr.), is obtained; this with $Fe(OAc)_2$, AcOH, and NaCl gives *hæmin III*, m. p. 269° (corr.), which depresses the m. p. of natural hæmin.

Re-investigation (cf. A., 1926, 1256) of the mixture of porphyrins (24% yield) formed when opsopyrrole and its carboxylic acid are heated with HCO_2H shows the presence of ætioporphyrin (12·3%), tetramethyltriethylporphinpropionic acids (40%) [a *Me* ester, m. p. 223° (corr.), is described], mesoporphyrins (27·3%) [Me_2 ester, m. p. 189° (corr.), described], a mixture of tricarboxylic acids (15·3%) [the mixture of Me_3 esters has m. p. 187—229° (corr.) (sinters at 167°)], and coproporphyrin [Me_4 ester, m. p. 176° (corr.)]. The imine obtained from opsopyrrolecarboxylic acid, anhyd. HCN, and HCl is converted by NaOEt and N_2H_4,H_2O at 160° into hæmopyrrolecarboxylic acid. 3 : 3′-*Dicarbethoxy*-4 : 5 : 4′ : 5′-*tetramethylpyrromethene* (*Cu* salt) has m. p. 166° (corr.). H. Burton.

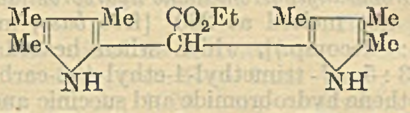
Porphyrin syntheses. XLII. Heptamethyl-β-carboxyethylporphin, a pyrromethene carbethoxylated on the connecting carbon, and pyrroles. H. Fischer and J. Hierneis (Annalen, 1931, 492, 21—35).—5-Aldehydo-2 : 3 : 4-trimethylpyrrole condensed with hæmo-, crypto-, and opso-pyrrolecarboxylic acids in EtOH–HBr gives 3 : 4 : 5 : 4′ : 5′-*pentamethyl*-3-′ (I), m. p. 235°, 3 : 4 : 5 : 3′ : 5′-*pentamethyl*-4′- (II), m. p. 207°, and 3 : 4 : 5 : 3′-*tetramethyl*-4′- (III), m. p. 228°, -β-*carboxyethylpyrromethene hydrobromides*, respectively, brominated in AcOH to 3 : 4 : 4′-*trimethyl*-5 : 5′-*di*(*bromomethyl*)-3′-, 3 : 4 : 3′-*trimethyl*-5 : 5′-*di*(*bromomethyl*)-4′-, and 5′-*bromo*-3 : 4 : 3′-*trimethyl*-5-*bromomethyl*-4′-β-*carboxyethylpyrromethene hydrobromides*, respectively. Fusion of (I) or (II) with 5 : 5′-dibromo-3 : 4 : 3′ : 4′-tetramethylpyrromethene hydrobromide (IV) (A., 1926, 1256) and succinic acid gives heptamethyl-3-β-carboxyethylporphin [*Me* ester, m. p. above 420° (*Cu* salt; *hæmin*)], also obtained unexpectedly from (III) and (IV).

Et 2 : 3 : 4-trimethylpyrrole-5-carboxylate and SO_2Cl_2 in Et_2O afford (after hydrolysis) *Et 2-aldehydo-* (V), m. p. 108° (*azine*, m. p. 260°), and *Et 2-carboxy-* (VI), m. p. 243°, -3 : 4-*dimethylpyrrole*-5-*carboxylates*. 2 : 3 : 4-Trimethylpyrrole (VII) and (V) give 5-carbethoxy-3 : 4 : 3′ : 4′ : 5′-pentamethylpyrromethene (as *hydrobromide*, m. p. 202°). Hydrolysis of (VI) with 10% NaOH affords 3 : 4-*dimethylpyrrole*-2 : 5-*dicarboxylic acid*; hydrolysis with 30% KOH and subsequent treatment with superheated steam gives 3 : 4-dimethylpyrrole. Et 3 : 4 : 5-trimethyl-2-pyrrylglyoxylate and (VII) with HBr (*d* 1·49) in EtOH or $COMe_2$ afford 3 : 4 : 5 : 3′ : 4′ : 5′-*hexamethylpyrrocarbethoxymethene hydrobromide* (VIII), m. p. 141°, whilst (VII), Et glyoxylate, and HBr (*d* 1·49) give 3 : 4 : 5 : 3′ : 4′ : 5′-*hexamethylpyrrocarbethoxymethane* (IX), m. p. 167°, and the hexamethylpyrromethene hydrobromide. Fusion of (VIII), 5 : 5′-dibromo-4 : 4′-dimethyl-3 : 3′-di-β-carboxyethylpyrromethene hydrobromide, and succinic acid yields 1 : 2 : 3 : 4 : 5 : 8-hexamethyl-6 : 7-di-β-carboxyethylporphin (A., 1930, 1449). (VII) and 2-*aldehydo*-3 : 4-*dimethylpyrrole*-5-*carboxylic acid*, m. p. 229° [by hydrolysis of (V)], give 5-carboxy-3 : 4 : 3′ : 4′ : 5′-pentamethylpyrromethene [as *hydrobromide*, m. p. 247° (decomp.)], whilst cryptopyrrole and Et 2-cryptopyrrylglyoxylate afford 3 : 5 : 3′ : 5′-tetramethyl-4 : 4-diethylpyrromethene.

(VIII.)

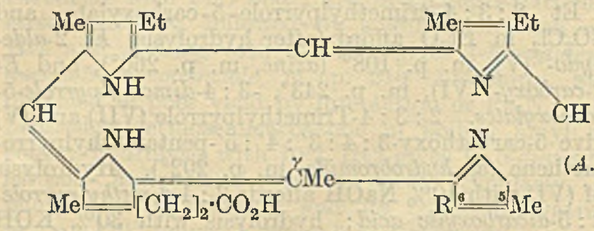


(IX.)



H. Burton.

Porphyrin syntheses. XLIII. Syntheses of 6-ethylphylloporphyrin and γ-methylmesoporphyrin. Chloroporphyrin e_4 (phylloporphyrin-6-carboxylic acid). H. Fischer and H. K. Weichmann (Annalen, 1931, 492, 35—65).—Xanthopyrrolecarboxylic acid, HCN, and HCl in Et_2O–$CHCl_3$ give β-(2-*aldehydo*-3-*methyl*-5-*ethyl*-4-*pyrryl*)*propionic acid*, m. p. 170° (corr.; all m. p. are corr. unless stated otherwise) (*semicarbazone*, m. p. 239°), which with opsopyrrole and 48% HBr in MeOH affords 3 : 3′-*dimethyl*-4 : 5′-*diethyl*-4′-β-*carboxyethylpyrromethene hydrobromide* (I), m. p. 187°. The 5-*Br*-derivative, chars gradually about 195°, of this, formed by bromination in AcOH, is brominated further in 90% HCO_2H to 5-*bromo*-3 : 3′-*dimethyl*-4-*ethyl*-5′-*bromoethyl*-4′-β-*carboxyethylpyrromethane hydrobromide* (II), not melted at 280°. Fusion of (I), 5-bromo-3 : 4′-dimethyl-4 : 3′-diethyl-5′-bromomethylpyrromethene hydrobromide (III), and methylsuccinic acid at 135—160° gives ætioporphyrin, tetramethyltriethylporphinmonopropionic acid III (IV), and about 1% of 6-*ethylphylloporphyrin* (V) (*A*, where R=Et)(*Me* ester, m. p. 275°) [also obtained from (II) and (III)]. Et opsopyrrolecarboxylate, AcCl, and $AlCl_3$ in CS_2 afford Et 5-*acetyl*-3-*methyl*-4-*ethylpyrrole*-2-*carboxylate*, m. p. 96°, reduced by N_2H_4,H_2O and NaOEt at 160° to 4-methyl-2 : 3-diethylpyrrole (VI), b. p. 95°/14 mm., which with HCN and HCl in Et_2O–$CHCl_3$ gives the *imine*



(*A*.)

hydrochloride, m. p. 183°, of *5-aldehydo-4-methyl-*2 : 3-*diethylpyrrole*, m. p. 70°. (VI), anhyd. HCO_2H, and 48% HBr furnish 3 : 3′-*dimethyl*-4 : 5 : 4′ : 5′-*tetraethylpyrromethene hydrobromide*, decomp. 180° (free *base*, m. p. 116°), converted by Br in (sun)light into a *compound*, $C_{19}H_{27}N_2Br_5$, not melted at 280°. The crude pyrromethene hydrobromide from (VI) and aldehydo-opsopyrrolecarboxylic acid is brominated in 95% HCO_2H to 5-*bromo*-4 : 3′-*dimethyl*-3 : 4′-*diethyl-5′-bromoethylpyrromethene hydrobromide*, darkens at 220°, not melted at 280° [free *base*, m. p. 150° (uncorr.; decomp.)], which when heated with 5′-bromo-3 : 5 : 3′-trimethyl-4-ethyl-4′-β-carboxyethylpyrromethene hydrobromide and succinic and methylsuccinic acids (1 : 2) at 135—170° affords (V) and mesoporphyrin V. (V) is converted by 30% MeOH–KOH in pyridine at 190—200° into (IV).

5′-Bromo-4 : 5 : 3′-trimethyl-3-ethyl-4′-β-carboxyethyl- and 5-bromo-3 : 3′-dimethyl-4 : 5′-diethyl-4′-β-carboxyethyl-pyrromethene hydrobromides (VII) fused with methylsuccinic acid give mesoporphyrin II and *γ-methylmesoporphyrin* (*mesophylloporphyrin*) (VIII) (*A*, where R=$\cdot[CH_2]_2\cdot CO_2H$) [*Me* ester, m. p. 245°, converted (about ½) by boiling with 18% HCl in O_2 for 3 hr. into mesoporphyrin].

The 5-*Br*-derivative, decomp. 228°, of 4-*carbethoxy*-3 : 4′ : 5′-*trimethyl-3′-ethylpyrromethene hydrobromide*, m. p. 208° (from hæmopyrrole and Et 2-aldehydo-3-methylpyrrole-4-carboxylate), fused with (VII) and methylsuccinic acid gives small amounts of phyllo-, pyrro-, and (mainly) rhodo-porphyrins; phylloporphyrin-6-carboxylic acid (chloroporphyrin e_4) is not isolated. Chloroporphyrin e_4 (IX) is unaffected by heating with succinic or methylsuccinic acid at 300° for 45 sec., or with methylsuccinic acid at 170° for 2 hr., whilst the Me esters of (V) and (VIII) are similarly converted into 1 : 3 : 5 : 8-tetramethyl-2 : 4 : 6-triethyl-7-β-carbomethoxyethylporphin and mesoporphyrin, respectively. (IX) is not affected by boiling 20% HCl in N_2 during 4 hr., whilst in O_2 it is oxidised to chloroporphyrin e_5 (formylrhodoporphyrin) (X) (the Me_2 ester, prepared by esterification with MeOH–HCl, had m. p. 310° and not 284°). (X) is converted by 18% HCl in O_2 into rhodoporphyrin-γ-carboxylic acid. The $\dot{:}C(\gamma)Me\cdot$ group (as in *A*) is termed the phyllo-principle.

Hæmopyrrolealdehyde and SO_2Cl_2 in Et_2O give, after hydrolysis with H_2O, opsopyrroledialdehyde; when the reaction proceeds energetically (no cooling), a *compound*, m. p. 159°, containing Cl and unaffected by NaOH, results. The methene from aldehydocryptopyrrolecarboxylic acid and opsopyrrole is brominated in AcOH to 5′-*bromo*-3 : 5 : 3′-*trimethyl*-4′-*ethyl*-4-β-*carboxyethylpyrromethene hydrobromide*, m. p. about 240° (uncorr.) with darkening and sintering. An improved method of prep. of 2 : 3′-dimethyl-4 : 4′-diethylpyrromethene hydrobromide is given. The *Me*, m. p. 140°, and *Et*, m. p. 86°, esters of 5-carbethoxy-4-methyl-2-ethyl-3-pyrrylmethylmalonic acid (XI) are prepared by the action of HCl on Et 4-methyl-2-ethylpyrrole-5-carboxylate and Me and Et methoxymethylmalonate, respectively. (XI), HCO_2H, and 48% HBr give a *mixture*, m. p. 171°, of 3 : 3′-dimethyl-5 : 5′-diethyl-4 : 4′-di-β-carboxyethyl- and -4 : 4′-di-ββ-dicarboxyethyl-pyrromethene hydrobromides.

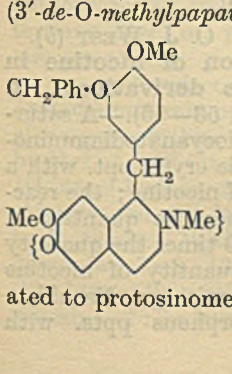
H. BURTON.

Chlorophyll series. VIII. Structure of chlorophyll *b*. J. B. CONANT, E. M. DIETZ, and T. H. WERNER (J. Amer. Chem. Soc., 1931, 53, 4436—4448; cf. A., 1931, 1310).—The methods developed for the elucidation of the structure of chlorophyll *a* have been applied to a study of chlorophyll *b* (I). The transformations in the *b* series closely parallel those in the *a* series and two simple rhodins have been obtained from which certain functional groups have been removed. The formation of semicarbazones shows that a CO group is present in the modified porphyrin ring in these rhodins and also throughout the *b* series. The explanation of allomerisation and the "phase test" reaction applies to the *b* as well as the *a* series. A variety of evidence thus leads to the conclusion that (I) is a keto-derivative of chlorophyll *a* in which a CO group connects two of the pyrrole rings in a modified porphyrin nucleus. Pure rhodin *g* (II) is best prepared by hot rapid saponification of pure methylphæophorbide *b* (III) (*semicarbazone*); pyrolysis of (II) in presence of talc and boiling Ph_2 gives pyrorhodin *g* (IV) (acid val. 12·5—13) and pyrorhodin *g*-porphyrin (V) (acid val. 3); two other compounds with acid vals. of about 1 and 8 are found in very small quantities. (IV) and (V) were not isolated as free acids, but as the corresponding *Me* esters, m. p. (block) 235° (*semicarbazone*) and 228—230°, respectively. Rhodin *g* Me_3 ester yields a *semicarbazone*. (II) and $K_3Mo(CN)_8$ give a rhodin *n* (Me ester, acid val. 18), which is being studied. Dehydrogenation of (III) with $K_3Mo(CN)_8$ gives a methyldehydrophæophorbide *b*, which was not isolated in a cryst. form and on rapid saponification, gives an unstable rhodin *i*; diazomethane converts this into the *Me_3* ester, m. p. 250—252°, of rhodin *k*, hydrolysed by 25% KOH in MeOH–Et_2O to the *Me* ester, m. p. 206°. Pyrolysis of the Me ester gives *rhodin* l *Me* ester, m. p. 187°, and *porphyrin* ll *Me* ester, which gives a *Me_2* ester, m. p. 185—187°. Hot saponification of rhodin *k* Me ester gives *rhodin* l (VI), and $(CO_2K)_2$; *rhodin* l *Me_2* ester yields a *semicarbazone*. Hot oxidative saponification of (III) gives the Me ester of (VI) and at least two other rhodins. Reduction of (VI) with N_2H_4 and NaOEt gives a small quantity of pyrroporphyrin and possibly rhodoporphyrin. Pyrolysis of (III) gives *methylpyrophæophorbide* b. Formulæ are proposed for (I), (II), (IV), and (VI).

C. J. WEST (*b*).

Synthetical experiments in the morphine group. I. R. ROBINSON and S. SUGASAWA (J.C.S., 1931, 3163—3172).—The blocked hydroaromatic structure of the morphine–thebaine–sinomenine group of alkaloids may have its biogenesis in a union of the two aromatic nuclei of a base of the laudanosine type. If the union occurs in such a position that loss of H with re-formation of a true aromatic nucleus is feasible, then an aporphine alkaloid results. If addition of one nucleus to the other occurs at a position already bearing a substituent, then loss of H is impossible without migration and a member of the morphine group is obtained. The phytosynthesis of thebaine from a protothebaine [8-hydroxy-7-methoxy-1-(3′-hydroxy-4′-methoxy)benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline] (*A*) by union of the nuclei, migration of H, oxide ring formation, and subsequent transposition of substituents, is discussed. Sinomenine can result from a protosinomenine [6-hydroxy-7-methoxy-1-(3′-hydroxy-4′-methoxy)benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline] (*B*). *A* and *B* could both arise from 2 mols. of 3-hydroxy-4-methoxyphenylalanine. Preliminary work on the synthesis of *B* is now described.

O-Benzyl*iso*vanillin (I) (improved prep.; cf. A., 1930, 785), hippuric acid, Ac_2O, and NaOAc at 100° give 2-*phenyl*-4-(3′-*benzyloxy*-4′-*methoxybenzylidene*)-*oxazolone*, m. p. 155°, hydrolysed by 10% NaOH to 3-*benzyloxy*-4-*methoxyphenylpyruvic acid*, m. p. 160—161°, which is oxidised by H_2O_2 in 2% KOH to 3-*benzyloxy*-4-*methoxyphenylacetic acid* (+H_2O), m. p. (anhyd.) 125°. (I), $MeNO_2$, Na_2CO_3, and NH_2Me,HCl in EtOH afford ω-*nitro*-3-*benzyloxy*-4-*methoxystyrene*, m. p. 127—128°, reduced electrolytically to β-3-benzyloxy-4-methoxyphenylethylamine (II) [*H oxalate*, m. p. 161°; *hydrochloride*, m. p. 166° (softens at 162°)]. (I) and $CH_2(CO_2H)_2$ in pyridine and piperidine give O-*benzylhesperetic* (3-*benzyloxy*-4-*methoxycinnamic*) *acid*, m. p. 179—180° (accompanied by the corresponding styrene), reduced to O-*benzyldihydrohesperetic acid*, m. p. 121—122° (the *Me* ester, m. p. 64°, is best prepared by benzylating Me dihydrohesperetate); the *amide*, m. p. 142°, could not be converted into (II) by the Hofmann method. *O*-Benzylhomo*iso*vanillyl chloride and (II) give O-*benzylhomoisovanillo*-β-3-*benzyloxy*-4-*methoxyphenylethylamide*, m. p. 118°, which could not be cyclised. O-*Benzylhomo*isovanillo-β-*methoxy*-β-*veratrylethylamide*, m. p. 124°, obtained from the above chloride and methoxyaminoethylveratrole (prep. from ω-nitro-3 : 4-dimethoxystyrene by addition of MeOH and subsequent reduction given), is cyclised by $POCl_3$ in PhMe to 6 : 7-*dimethoxy*-1-(3′-*benzyloxy*-4′-*methoxy*)*benzyl*isoquinoline (III), m. p. 112—113° (*picrate*, m. p. 192°; *methiodide*, m. p. 230—231°), and some of the 3′-*hydroxy*-derivative (3′-*de*-O-*methylpapaverine*), m. p. 181—182°. The methosulphate of (III) is hydrolysed by aq. $Ba(OH)_2$ to *anhydro*-6-*hydroxy*-7-*methoxy*-1-(3′-*benzyloxy*-4′-*methoxy*)*benzyl*-iso*quinoline methohydroxide* (annexed formula), m. p. 239—240°, which with HCl gives a methochloride, m. p. 242°, reduced catalytically (PtO_2) in 90% EtOH to a product which is debenzylated to protosinomenine (not yet obtained cryst.).



H. BURTON.

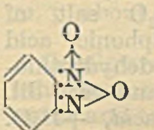
Synthetic experiments in the morphine group. II. Derivatives of diphenyl ether. R. ROBINSON and S. SUGASAWA (J.C.S., 1931, 3173—3176).—Possible intermediates in the synthesis of 3 : 3′-oxido-di-(*p*-methoxyphenylalanine) are described. 2 : 2′-Dimethoxydiphenyl ether (I) (improved prep.; cf. A., 1906, i, 258) is converted by the Gattermann method into 2 : 2′-*dimethoxy*-5 : 5′-*diformyldiphenyl ether* (II), m. p. 136° (*dioxime*, m. p. 192°), also prepared from *iso*vanillin, 2-bromoanisaldehyde, Cu-bronze, K_2CO_3, and pyridine at 190°. The yields of (II) are poor. (II), hippuric acid, Ac_2O, and NaOAc at 100° (bath) give *dianhydro*-(2 : 2′-*dimethoxy*-5 : 5′-*diformyldiphenyl ether*) *bis*-2-*phenyloxazolone*, m. p. 223—225°. (I) and HNO_3 (*d* 1·42) in AcOH afford some 5 : 5′-*dinitro*-2 : 2′-*dimethoxydiphenyl ether*, m. p. 174°; the NH_2 groups in the corresponding diamine could not be replaced by CN. The K salt of Et *iso*vanillate heated with 2-bromoanisaldehyde, Cu-bronze, and $Cu(OAc)_2$ at 170—180° gives, after hydrolysis with EtOH–KOH, 2 : 2′-*dimethoxy*-5-*formyl*-5′-*carboxydiphenyl ether*, m. p. 212° (sinters at 208—209°).

H. BURTON.

Chromanoquinoline derivatives. J. ALGAR and T. A. M'CULLAGH (Proc. Roy. Irish Acad., 1931, **40**, B, 84—89; cf., A., 1929, 349).—*o*-Hydroxybenzylideneacetophenone, *o*-nitrobenzaldehyde, and HCl in EtOH give o-*nitrobenzylideneflavanone*, m. p. 155·5—156·5°, reduced in AcOH with $SnCl_2$ and HCl to 2 : 5-(2-*phenylchromano*-3 : 4)-*quinoline*, m. p. 178—179° (yield 40%). Similarly, *o*-hydroxyanisylideneacetophenone gives o-*nitrobenzylidene*-4′-*methoxyflavanone*, m. p. 149—150°, and 2 : 3-(2-*anisylchromano*-3 : 4)-*quinoline*, m. p. 165—166° (yield 50%), whilst *o*-hydroxypiperonylideneacetophenone gives o-*nitrobenzylidene*-3′ : 4′-*methylenedioxyflavanone*, m. p. 179·5—180·5° (yield 70%), and 2 : 3-(2-*piperonylchromano*-3 : 4)-*quinoline*, m. p. 177—178° (small yield).

A. A. LEVI.

Constitution of benzfurazan and benzfurazan oxide. D. L. HAMMICK, W. A. M. EDWARDES, and E. R. STEINER (J.C.S., 1931, 3308—3313).—Benzfurazan oxide (I) with Br in CS_2 gives two isomeric *forms*, m. p. 170° and m. p. 117° of *tetrabromotetrahydrobenzfurazan oxide*, both converted by aq. KOH into the same *dibromofurazan oxide*, m. p. 132° (II). Similarly, benzfurazan [by reduction of (I) with 4% KOH in MeOH] affords *tetrabromotetrahydrobenzfurazan*, m. p. 147°, converted into *dibromobenzfurazan*, m. p. 113°, identical with a specimen obtained by reduction of (II) with NH_2OH. These results indicate a quinonoid structure (I) for benzfurazan and its oxide as originally suggested by Green and Rowe (J.C.S., 1912, **101**, 2452), a view which is confirmed by determinations of the parachor of benzfurazan, 252·2, its oxide, 274·3, and tolufurazan oxide, 311·4. The formation of the same furazan oxide from *o*-nitroazoimide or *o*-nitroaniline substituted in the 4- or 5-positions may be due to the conversion of an unstable oxide into a stable isomeride through the *s*-*o*-dinitroso-form in the liquid state.



(I.)

J. W. BAKER.

Isatogens. VIII. Isatogens from 4 : 6-dinitro-*m*-xylene. P. RUGGLI and R. THOUVAY

(Helv. Chim. Acta, 1931, **14**, 1256—1265).—The *dichloride* (I), m. p. 181°, and *tetrachloride* (II), m. p. 158°, of 4 : 6-dinitro-1 : 3-distyrylbenzene (III) (this vol., 56) are converted by boiling pyridine into 4 : 6-*dinitro*-3-*styryl*-1-α-*chlorostyryl*-, m. p. 181°, and 4 : 6-*dinitro*-1 : 3-*di*-α-*chlorostyryl-benzene* (IV), m. p. 145°, respectively. When a solution of (II) in cold pyridine is exposed to sunlight or ultra-violet light, 6-*nitro*-2-*phenyl*-5-α-*chlorostyrylisatogen* (V), m. p. 243°, is produced after 3—10 days; a trace of (V) is also formed during the prep. of (IV). (V) is converted by NH_2·NHPh in EtOH into 6-*nitro*-2-*phenyl*-5-α-*chlorostyrylindoxyl*, m. p. 203°. (I) is converted [as (II)] into 6-*nitro*-2-*phenyl*-5-*styrylisatogen* (VI), m. p. 233—234°, chlorinated in $C_2H_2Cl_4$ to (probably) the 5-β-*chlorostyryl* derivative, m. p. 247°. The *tetrabromide*, m. p. 206°, of (III) and boiling pyridine give 4 : 6-*dinitro*-3-*styryl*-1-α-*bromostyrylbenzene*, m. p. 173°, convertible [as (II)] into (VI). (IV) is stable to light when dissolved in pyridine. H. BURTON.

Monoarylguanidines. III. Benzthiazolylguanidine. G. B. L. SMITH, C. W. MASON, and R. H. CARROLL (J. Amer. Chem. Soc., 1931, **53**, 4103—4109; cf. A., 1929, 1186).—*o*-NH_2·C_6H_4·SH (Zn salt) and dicyanodiamidine in 95% EtOH and conc. HCl give the *hydrochloride*, m. p. 239—241°, of *benzothiazolylguanidine* (I), m. p. 175—176° (*Ac_2* derivative; *sulphate*, m. p. 294—295°; *nitrate*, m. p. 236—239°; *picrate*, m. p. 280—289°). Crystallisation of (I) from H_2O by cooling rapidly gives an anhyd. (plates) form, m. p. 175—176°, whilst slow crystallisation gives a *monohydrate*, m. p. 175—176°; crystallographic data are given for the several forms of (I). Potentiometric titration shows that (I) is a very weak base. The third cryst. modification, obtained when the molten base is supercooled, is believed to be a tautomeric form of (I). C. J. WEST (*b*).

Search for trypanocidal activity. Derivatives of dehydrothio-*p*-toluidinesulphonic acid and of 3-aminocarbazoledisulphonic acid. G. T. MORGAN and J. G. MITCHELL (J.C.S., 1931, 3279—3283).—Reduction of the *Na* $+3H_2O$ salt of 3-nitrobenzoyldehydrothio-*p*-toluidinesulphonic acid [by *m*-NO_2·C_6H_4·COCl and NaOH on dehydrothio-*p*-toluidinesulphonic acid (I)] with Fe and very dil. HCl gives the corresponding 3-*amino-acid*, $+H_2O$. This is converted by $COCl_2$ in aq. Na_2CO_3 suspension into the *ureido*-derivative, purified as its *Na* $+5H_2O$ salt. (I) similarly gives *ureidodehydrothio*-p-*toluidinesulphonic acid* (*Na* $+6H_2O$ salt), whilst *sulphodehydrothiotoluene*-p-*arsinic acid* (Na salt) is obtained by the Bart reaction. Reduction of the *Ca* salt of 3-nitrocarbazoledisulphonic acid (best obtained by sulphonation of 3-nitrocarbazole with conc. H_2SO_4 at 70—75°) with Fe and very dil. HCl gives the 3-*amino-acid* (II) in poor yield; therefore the reduction product was treated directly with 2-nitro-*p*-toluoyl chloride and NaOH to give 3-(3′-*nitro*-4′-*methylbenzamido*)*carbazoledisulphonic acid* (III) (*Na* salt), similarly reduced and converted by *m*-NO_2·C_6H_4·COCl into 3-(3′-3″-*nitrobenzamido*-4′-*methylbenzamido*)*carbazoledisulphonic acid* (IV) (*Na* salt). Reduction of III with $FeCl_2$ and NaOH and of (IV) with Fe and very dil. HCl, and subsequent phosgenation gives, respectively, *ureido*-3-(3′-*amino*-4′-*methylbenzamido*)- (*Na* salt) and -3-(3′-3″-*amino*-*benzamido*-4′-*methylbenzamido*)- (*Na* salt) -*carbazoledisulphonic acid*; *ureido-3-aminocarbazoledisulphonic acid* (*Na* salt) is similarly prepared from $COCl_2$ and (II). None of these derivatives exhibits trypanocidal activity. J. W. BAKER.

Thiazines. I. Syntheses in the *peri*naphtho-*m*-thiazine group. M. T. BOGERT and J. H. BARTLETT (J. Amer. Chem. Soc., 1931, **53**, 4046—4057).—Reduction of 1 : 8-ClO_2S·$C_{10}H_6$·NO_2 by $SnCl_2$ and HCl in AcOH gives 79% of 8-*thiol*-α-*naphthylamine chlorostannate* (I); if the reaction product is refluxed for 6—7 min., the product is the additive *compound* of $SnCl_4$ and 8-thiolacet-α-naphthalide (II), which is more stable than (I). (II) in EtOH–NaOH, or, better, in AcOH–NaOAc with Ac_2O, gives 2-*methyl*-peri*naphthothiazine* (III), m. p. 96·5—97·5° (all m. p. are corr.), in yields of 15 and 93%, respectively. (III) and PhCHO in EtOH–NaOH give 45% of the 2-*styryl* derivative, m. p. 132—133°. (III), *o*-$C_6H_4(CO)_2O$, and $ZnCl_2$ give 27% of the *phthalone*, amorphous, m. p. 173·5—174·5°, which with conc. H_2SO_4 affords a pale brown analogue of quinoline-yellow; this dyes wool a bright yellow and resembles its analogue in fastness to light, laundering, and bleeding. (I), decomposed with AcOH and NaOAc and treated with *o*-NO_2·C_6H_4·COCl, gives a mixture of the NS-*di*-o-*nitrobenzoyl* (IV), m. p. 185·5—186·5° (decomp.), and the N(?) -o-*nitrobenzoyl* derivatives, amorphous, m. p. about 225° (decomp.), of 8-thiol-α-naphthylamine; either derivative with AcOH and NaOAc gives 2-o-*nitrophenyl*peri*naphthothiazine*, m. p. 166—168°, reduced by $SnCl_2$ and HCl in EtOH to the o-*amino*-derivative, m. p. 154—154·5° [also formed by reduction of (IV)]. The NS-*di*-m-*nitrobenzoyl* (V), m. p. 185·5—186·5° (decomp.), and -*di*-p-*nitrobenzoyl* derivatives, m. p. 248—249° (decomp.), of 8-thiol-α-naphthylamine are prepared similarly from (I), or, better, from (II). (I), AcOH, NaOAc, and *m*-NO_2·C_6H_4·COCl at 60° give 55% of 2-m-*nitrophenyl*peri*naphthothiazine*, m. p. 182·5—183°, also formed from (V), NaOAc, and AcOH, reduced to the 2-m-*aminophenyl* derivative, m. p. 148—149°. 2-p-*Nitro*-, m. p. 208·5—209°, and 2-p-*amino-phenyl*peri*naphthothiazines*, m. p. 143—143·5°, are also prepared. 2-m-, m. p. 186°, and 2-p-, m. p. 217—219°, -*hydroxyphenyl*peri*naphthothiazines* are prepared by the diazo-reaction. Chloramine-yellow dyes are prepared from the *m*- and *p*-NH_2-derivatives and their dyeing properties tested. In method of synthesis, structure, and properties, these new products resemble the benzthiazoles.

C. J. WEST (*b*).

Microchemical determination of nicotine in presence of pyridine and its derivatives. R. HOFMANN (Mikrochem., 1931, **10**, 53—56).—A saturated solution of hydroxotrithiocyanatodiamminochromic acid gives a characteristic cryst. ppt. with a neutral or slightly acid solution of nicotine; the reaction is sp. in presence of 3 times the quantity of pyridine, lutidine, or picoline, or 9 times the quantity of collidine, and the smallest quantity of nicotine which can be detected is 0·157 microg. Na silicotungstate normally yields amorphous ppts. with alkaloids, but if a solution of the salt is added to a nicotine solution of such concn. that slight turbidity only is produced, and a crystal of NaCl is then introduced, a characteristic cryst. ppt. separates within 5—10 min.; the limit of sensitivity is 0·4 microg. Pyridine yields similar crystals, which, however, may be differentiated by using polarised light. The methylpyridines do not form characteristic ppts.

H. F. GILLBE.

Alkaloids of tobacco. M. EHRENSTEIN (Arch. Pharm., 1931, **269**, 627—659).—" Nicoteine " (A., 1901, i, 339), from extracts of Kentucky tobacco, is a mixture of *nornicotine* (I) and *l*-2-(β-pyridyl)piperidine (II), separated by distillation, and fractionation of the picrates. Previous specimens of (I) (A., 1930, 1444) were partly racemised or impure. (II) is possibly identical with anabasine (A., 1931, 498). (I), b. p. 130·5—131·3°/11 mm., miscible with H_2O, $[\alpha]_D^{20}$ —17·7° (base), +9·19° (in *N*-HCl) [*dipicrate*, m. p. 191—192°; *dipicrolonate*, m. p. 250—252° (decomp.); *-carbamide*, m. p. 167—170°; *-phenylthiocarbamide*, m. p. 176—177·5°], gives nicotine methiodide on exhaustive methylation, nicotinic acid when oxidised with HNO_3, and 2-(3-*pyridyl*)*pyrrole*, m. p. 100—102° (*picrate*, m. p. 202—203°), when dehydrogenated by Pt–asbestos at 320—330°. (II), b. p. 137—138·5°, $[\alpha]_D^{18\cdot5}$ —72·59° (base), —14·69° (in *N*-HCl) [*dipicrate*, m. p. 201—204·5°; *dipicrolonate*, m. p. 233—235° (decomp.); *-carbamide*, m. p. 182—185°; *-phenylthiocarbamide*, m. p. 162—164°], with hot conc. HNO_3 gives ?-*nitro*-2 : 3′-*dipyridyl*, m. p. 154·5—155°, and nicotinic acid; with KOH and MeI in MeOH it yields l-2-(β-*pyridyl*)-N-*methylpiperidine methiodide*, m. p. 212—214° after decomp. from 209°, and when dehydrogenated 2 : 3′-*dipyridyl*, b. p. 158—160°/19 mm., insol. in H_2O [*picrate*, m. p. 168—170° (once obtained with m. p. 148—151°; lit. 149°); *picrolonate*, m. p. 243—244·5° (decomp.)]. 3 : 3′-Dipyridyl is sol. in H_2O and has b. p. 173—175°/70 mm. (picrate, new m. p. 235—236°). When kept with MeI in MeOH, (II) gives the impure N-*Me* derivative (III), b. p. 135—138°/18 mm. [*dipicrate*, m. p. 213—214°; *dipicrolonate*, amorphous, m. p. 230—231° (decomp.)], and an oil, from which by treatment with KOH and distillation a little (III) was obtained.

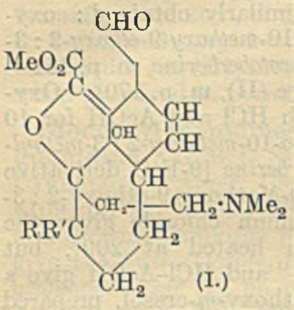
R. S. CAHN.

Berberrubine, palmatrubine, and similar compounds. IV. Alkaloids of columba root. K. FEIST and W. AWE (Arch. Pharm., 1931, **269**, 660—678; cf. A., 1925, i, 830).—Even when washed with alkali, palmatine contains jatrorrhizine and a phenolic *base*, $C_{20}H_{19}O_4N$ (*hydriodide*, m. p. 228°), reduced by Zn and H_2SO_4 to an amorphous, phenolic, tertiary *base*, m. p. 135—137°. Palmatine gives a *thiocyanate*, m. p. 210° (decomp.), and *perchlorate*, m. p. 262° (decomp.). Palmatine chloride, when heated alone or in petroleum (b. p. above 200°) at 190°, gives *palmatrubine* (I), m. p. about 300°, converted by MeI at 100° into palmatine iodide, and by HCl and HI into 9-*hydroxy*-2 : 3 : 10-*trimethoxyprotoberberinium chloride* and *iodide* (m. p. of the latter 224—228°), respectively. With Zn, dil. H_2SO_4, and AcOH (I) gives the 7 : 8 : 13 : 14-tetrahydro-base, m. p. 150° (lit. 148—149°), and with EtI or NaOH and Me_2SO_4 affords 2 : 3 : 10-*trimethoxy*-9-*ethoxyprotoberberinium iodide*, m. p. 227—230° (decomp.), which after conversion into the nitrate is reduced by Zn, dil. H_2SO_4, and AcOH to the 7 : 8 : 13 : 14-tetrahydro-base, m. p. 116° (lit. 115°). Jatrorrhizine chloride when heated at 190° in an atm. of CO_2 gives *jatrorrhizrubine*, reduced as usual to 3 : 9-*dihydroxy*-2 : 10-*dimethoxy*-7 : 8 : 13 : 14-*tetrahydroprotoberberine*, m. p. 164°. 8-Phenyldihydroberberine, m. p. 196° (lit. 195°) (modified prep.), when oxidised by $Hg(OAc)_2$ in AcOH and treated with HCl, affords 8-*phenylberberine chloride*, m. p. about 270° (decomp.) [*iodide*, m. p. 276° (decomp.)], reduced to 8-phenyltetrahydroberberine, m. p. 222°, and converted by heating at 250° in an atm. of CO_2 into MeCl and 8-*phenylberberrubine*, m. p. 173° (*hydrochloride*). Palmatine chloride and hot aq. NaOH give dihydropalmatine and oxypalmatine, and the following substances were similarly obtained: oxy- and dihydro-berberine; 10-*methoxy*-9-*ethoxy*-2 : 3-*methylenedioxy*-7 : 8-*dihydroprotoberberine*, m. p. 151—153°, and its 8-*keto*-derivative (II), m. p. 170°. Oxyberberine, when heated with HCl and AcOH for 10 min., yields 9-*hydroxy*-8-*keto*-10-*methoxy*-2 : 3-*methylenedioxy*-7 : 8-*dihydroprotoberberine* [9-EtO derivative of (II)], m. p. 248°. 10-Methoxy-9-ethoxy-2 : 3-methylenedioxyprotoberberinium chloride gives the corresponding rubine when heated at 200°, but " ruboxyberberine Et ether " and HCl–AcOH give a substance, m. p. 320°. 2-Ethoxy-*m*-cresol, prepared from 3-nitro-*o*-cresol by way of 3-nitro-2-ethoxytoluene and 2-ethoxy-*m*-toluidine (modified preps.), with Me_2SO_4 and 10% aq. KOH gives 3-*methoxy*-2-*ethoxytoluene*, b. p. 98—103°/20 mm., which with AcCl and $AlCl_3$ in CS_2 at 50—60° affords ?-*aceto*-3-*methoxy*-2-*ethoxytoluene* [*methoxyethoxyacetophenone*] (III), b. p. 170—180°/20 mm. (*oxime*, m. p. 123°; *semicarbazone*, m. p. 149°, solidifying on further heating and remelting at 231°), oxidised by NaOI to a *methoxyethoxytoluic acid*, m. p. 115°, further oxidised by alkaline $KMnO_4$ to 4-methoxy-3-ethoxyphthalic acid and two *acids*, m. p. 246° and 183°. The same three acids were obtained when (III) was treated with alkaline $KMnO_4$ and the resulting *keto-acid*, $C_{12}H_{14}O_5$, m. p. about 130°, was further oxidised with $KMnO_4$.

R. S. CAHN.

Configuration of optically active α-phenylethylamine and of bases of the type of laudanosine and tetrahydroberberine. W. LEITHE (Ber., 1931, 64, [*B*], 2827—2832; cf. A., 1930, 1049).—Successive nitration, reduction, diazotisation, and treatment with boiling H_2O of *l*-*N*-benzoyl-α-phenylethylamine followed by oxidation with CrO_3 in AcOH leads to alanine, isolated as *l*(+)-benzoylalanine, identical with that prepared from natural *l*(+)-alanine. (—)-α-Phenylethylamine has therefore the *l*-configuration. Determination of the configuration of bases of laudanosine and canadine type with respect to *l*(+)-alanine is justifiable, since the asymmetric centres in the compounds are similarly constructed, all including a H atom, a C_6H_6 nucleus, an amine-like N, and a Me residue. Direct degradation is impossible and comparison is made of the effect of salt formation and neighbouring mols. (solvent) on optical activity. The sp. rotations of *l*-phenylethylamine, *l*-*N*-ethylphenylamine, *l*-1-methyltetrahydro*iso*quinoline, *l*-protolaudanosine, and *l*-tetrahydroprotoberberine in substance, in *cyclo*hexane, $CHCl_3$, and EtOH, and as salt in H_2O are recorded. The following configurations are assigned in the sense of the Wohl–Freudenberger system; the opium bases *l*(in $CHCl_3$+)-laudanosine, *l*(+)-codamine, *d*(—)-laudanidine : *l*(—)-canadine from *Hydrastis canadensis*; the *Corydalis* alkaloids *d*(+)-tetrahydropalmatine, *d*(+)-corypalmine, *d*(+)-canadine, and *d*(+)-tetrahydrocoptisine : *l*(—)-sinactine from *Sinomenium acutum*. H. WREN.

Action of ozone on de-*N*-methyldihydrocodeine. I. E. SPEYER and K. KOULEN (Ber., 1931, **64**, [*B*], 2815—2819).—*De*-N-*methyldihydrocodeine hydrochloride* in H_2O is transformed by O_3 into "*de*-N-*methyl*-7 : 8-*dihydrocodizal*-3-*methyl ester* (I; R=H, R′=OH), m. p. 205—206°, $[\alpha]_D^{18}$ —101·4° in dil. AcOH (*oxime*, decomp. 220°; *hydriodide*, slow decomp. 250°; *methiodide*, decomp. above 290°; *Ac* derivative and its *hydriodide*, m. p. 234—235°). In presence of colloidal Pd and 2% AcOH the ester is hydrogenated to *de*-N-*methyl*-4 : 5 : 7 : 8-*tetrahydrocodizal*-3-*methyl ester*, m. p. 175—176°, $[\alpha]_D^{18}$ —56·8° in dil. AcOH. The dihydro-ester is oxidised by $Na_2Cr_2O_7$ and 5% AcOH to *de*-N-*methyl*-7 : 8-*dihydrocodizonal*-3-*methyl ester*" (I; R+R′=O), m. p. 172°, $[\alpha]_D^{18}$ —18·0° in dil. AcOH (*hydrochloride*, slow decomp. above 268°). H. WREN.



(I.)

Lupin alkaloids. V. G. R. CLEMO, G. R. RAMAGE, and R. RAPER (J.C.S., 1931, 3190—3200).—Prolonged interaction of Me lupininate and N_2H_4,H_2O at 100° gives *lupininhydrazide*, m. p. 118—119°, converted by amyl nitrite in EtOH–HCl into the *hydrochloride*, m. p. 277—278° (decomp.), of *methylnorlupinanylurethane*, b. p. 125—128°/1 mm., which with conc. HCl affords *aminonorlupinane* (I), b. p. 73—75°/1 mm. (I) and HNO_2 give (mainly) d-*norlupinene* (II), b. p. 40—43°/1 mm., $[\alpha]_D$ +33·7° in $COMe_2$ [*picrate*, m. p. 175°; *methiodide*, m. p. 308—310° (decomp.)], some *hydroxynorlupinane*, b. p. 68—72°/1 mm., and other bases, b. p. 100—120°/1 mm. [a *picrate*, $C_{15}H_{27}O_3N_3,C_6H_3O_7N_3$, m. p. 207—208° (decomp.), is isolated]. Catalytic reduction (Pd–charcoal) of (II) in AcOH affords norlupinane, b. p. 43—45°/1 mm. (α=0), identical with the base obtained (A., 1931, 499) by distilling lupininic acid with soda-lime. 1-Keto-octahydropyridocoline, $CH_2Cl·CO_2Et$, and $NaNH_2$ in Et_2O give *Et* β-1-*octahydropyridocolylglycidate*, b. p. 152°/0·1 mm.; the free acid (or the corresponding aldehyde by loss of CO_2) could not be isolated. Et piperidine-2 : 3-dicarboxylate, $CH_2Br·CH_2·CH_2·CN$, and K_2CO_3 at 100° (bath) afford, after treatment with EtOH–HCl, *Et* γ-2 : 3-*dicarbethoxypiperidinobutyrate*, b. p. 160—166°/0·1 mm. This undergoes the Dieckmann reaction; the resulting product after hydrolysis with HCl (loss of CO_2), Clemmensen reduction, and esterification (MeOH) gives *Me octahydropyridocoline*-1-*carboxylate* (III), b. p. 102—105°/0·5 mm. (*picrate*, m. p. 187°). If the above product is hydrolysed and then esterified a considerable amount of 1-keto-octahydropyridocoline (IV) [semicarbazone, m. p. 230° (lit. 215°)] is obtained in addition to Me 9-keto-octahydropyridocoline-1-carboxylate. Octahydropyridocoline does not occur in *cis*- and *trans*-forms, since the same product is produced by reduction of (IV) (occurring as a by-product) irrespective of the configuration of the starting materials. Me lupininate heated with aq. NH_4 *d*-bromocamphorsulphonate furnishes the cryst. *Me lupininate* d-*bromocamphorsulphonate*, m. p. 171—173°, whilst (III) does not react. Reduction (Bouveault) of (III) gives an oil which affords a non-cryst. tartrate, whilst lupinine furnishes a d-*tartrate*, m. p. 171°. These results show that lupinine does not possess the structure assigned by Karrer *et al.* (A., 1929, 200).

Oxidation of oxylupanine with aq. $KMnO_4$ at 40—50° gives a *substance* "*A*," $C_{15}H_{22}O_3N_2$, m. p. 212°, hydrolysed by aq. $Ba(OH)_2$ at 270° to glutaric acid, a *compound* (V), $C_{10}H_{20}O_4N_2$, a substance (VI) (*picrate*, m. p. 231°), and a trace of a compound (picrate, decomp. 290°). Glutaric acid, (V), and (VI) are also formed from oxylupanine and aq. $Ba(OH)_2$ at 270°. The substance recovered when "*A*" is treated with SO_2 in H_2O, the solution boiled, and then evaporated, has the same composition as "*A*," but shows a variable m. p. (144—157°). A small amount of *compound* "*B*," m. p. 233°, isomeric with "*A*," is produced as a by-product in the oxidation of lupinine (cf. A., 1928, 1030). A partial structure is suggested which explains the introduction of O without loss of H (as in the formation of "*A*"). H. BURTON.

New *Aconitum* alkaloid. R. MAJIMA and S. MORIO (Proc. Imp. Acad. Tokyo, 1931, **7**, 351—352).—A new alkaloid, *lucidusculine*, $C_{24}H_{37}O_4N$, has been isolated from *A. lucidusculum*. The base and most of its salts, in contrast to the known *Aconitum* alkaloids, is cryst. and has greater optical activity. It combines with MeI, forms a picrate, and with KOH–EtOH loses an Ac group, forming *luciculine*, $C_{22}H_{35}O_3N,H_2O$, from which the H_2O cannot be abstracted. Lucidusculine has no OMe-group, but probably 2 OH and a NMe groups. It is suggested that the compound, $C_{22}H_{31}O_2N,H_2O$ obtained from atisine by Jowett (J.C.S., 1896, **69**, 1518) is probably related to luciculine. F. R. SHAW.

Formulæ of three opium derivatives. D. B. DOTT (Pharm. J., 1931, **127**, 520—521).—Cryst. codeine sulphate does not ordinarily effloresce and the anhyd. salt gains $3H_2O$ in air, whereas the corresponding ethylmorphine salt gains $5H_2O$. Ethylmorphine may be distinguished from codeine by the cryst. ppt. which is formed when 0·1 g is dissolved in H_2O, 8 c.c., and shaken with 4 drops of conc. aq. KOH (codeine: no ppt.). Cryst. cotarnine hydrochloride, $C_{12}H_{13}O_3N,HCl,2\frac{1}{2}H_2O$, becomes anhyd. at 98°. The m. p. (130°) of cotarnine should be determined quickly, as the alkaloid melts slowly at temp. lower than 100°, possibly due to oxidation. E. H. SHARPLES.

Strychnine and brucine. XIV. Oxidation of hexahydrostrychnine. L. H. BRIGGS and R. ROBINSON (J.C.S., 1931, 3160—3163).—Oxidation of hexahydrostrychnine (improved prep.; cf. A., 1927,

1208) with CrO_3 in dil. H_2SO_4 at 16—80° gives 22% of an *acid* (I), $C_{21}H_{22}O_4N_2$ ($+2H_2O$), m. p. 281—282° (decomp.), $[\alpha]_D^{20}$ +10·73° in 1% HCl [*methosulphate*, not melted at 318°; *methiodide*, m. p. 280—287° (decomp.); *methochloride*, darkens at 280° and begins to melt at 320°], which may result from the change $C_{17}H_{19}ON(CH{\cdot}CH)(CH_2{\cdot}OH\,NH)(Me) \longrightarrow C_{17}H_{19}ON(CH{\cdot}CH)(CO{\cdot}N)(CO_2H)$. The changes involved may be more complex, since (I) does not exhibit the usual strychnine colour reaction with H_2SO_4 and a dichromate. (I) probably contains the original $\vdots N(a){\cdot}CO{\cdot}CH_2{\cdot}$ group of strychnine, since it gives a benzylidene derivative (*picrate*). The acid, $C_{21}H_{22}O_4N_2$, described by Leuchs (A., 1931, 242) is probably $C_{21}H_{20}O_4N_2$; it is reduced catalytically (Pd–charcoal) to (I), which is identical with the acid, $C_{21}H_{24}O_4N_2$, prepared by Leuchs and Beyer (A., 1931, 1312). H. BURTON.

***Strychnos* alkaloids. VI. Typical colour reactions.** H. WIELAND, F. CALVET, and W. W. MOYER (Annalen, 1931, **491**, 107—116).—All derivatives of vomicine in which the original lactam ring has been opened (except bromo- and bromodihydro-vomicinic acids) are oxidised by CrO_3 in dil. acid to dyes, which are postulated as diphenoquinonediimonium dicarboxylates; the failure of the above Br derivatives to undergo this change is due to the *p*-configuration of the Br atom and ·NH· group. The above also applies to the analogous strychnine derivatives but not to the brucine compounds (OMe group *para* to ·NH·). The dyes are reduced to colourless intermediates which, when warmed (lactamisation) with the dil. acid, afford lactams (when possible) of the corresponding benzidine dicarboxylates. The original mol. is doubled during the process. Thus, vomicinic acid and CrO_3 (= 2O) in cold *N*-HCl give a violet dye (not isolated), reduced by SO_2 or Zn dust to *didehydrovomicine* (*divomicyl*) (I), $C_{44}H_{46}O_8N_4$, not melted at 320° (darkens at 250°); $FeCl_3$, $Br–H_2O$, and H_2O_2 can be used instead of CrO_3. (I) is not re-oxidised to the violet dye, but the solution obtained by hydrolysis with EtOH–KOH is readily autoxidised (blue coloration). Strychnidine is converted through a red dye into *didehydrostrychnidine* (*distrychnidyl*), $C_{42}H_{46}O_2N_4$, not melted at 320°, re-oxidised to the dye. Tetrahydrostrychnine gives a brownish-red dye convertible into *didehydrotetrahydrostrychnine* (*ditetrahydrostrychnyl*), $C_{42}H_{50}O_2N_4$, not melted at 300° (darkens above 260°), whilst *ON*-dimethylvomicinic acid affords a bluish-violet dye reduced to an *acid*, $C_{48}H_{58}O_{10}N_4$ ($+8H_2O$), decomp. above 300° (*Me_2 ester*, m. p. 214—220°). Most of the above compounds separate from pyridine with solvent of crystallisation which is lost at 150—180°/vac.

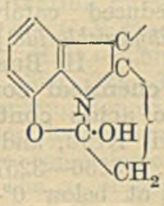
The formula $C_{42}H_{42}O_8N_4$ is suggested for the acid, $C_{21}H_{22}O_4N_2$, obtained by Leuchs (A., 1931, 242) by CrO_3 oxidation of tetrahydrostrychnine. Partial formulæ are suggested. H. BURTON.

***Strychnos* alkaloids. VII. Methylation of vomicinic acid and derivatives of vomicine.** H. WIELAND and F. CALVET. **VIII. Vomicidine.** H. WIELAND and W. W. MOYER. **IX. Oxidation of vomicine and dihydrovomicine with chromic acid.** H. WIELAND, F. HÖLSCHER, and F. CORTESE. **X. Nitrations in the vomicine group.** H. WIELAND and F. HÖLSCHER (Annalen, 1931, **491**, 117—129, 129—133, 133—148, 149—161).—VII. Vomicinic acid and MeI in MeOH–KOH and H_2 at room temp. give *ON-dimethylvomicinic acid* (I), $C_{24}H_{30}O_5N_2$ ($+2H_2O$), m. p. 242—244° after loss of H_2O at 170°, its *Me* ester (II), m. p. 214—216°, $[\alpha]_D^{20}$ +61·7° in EtOH, and *N*-methylvomicinic acid (III); (I) is identical with the substance previously described as vomicinic acid betaine (A., 1929, 708), and is usually isolated as its *hydriodide*, m. p. 185—200° (with loss of H_2O). When the methylation is carried out first at room temp. and then in the hot, (I), (II), and the *Me* ester, m. p. 262—266° (decomp.), $[\alpha]_D^{20}$ +38·6° in EtOH, of (III) are produced. In one experiment an alkali-insol. *methylvomicine*, m. p. 286—290° (decomp.), $[\alpha]_D^{20}$ +16·4° in EtOH (demethylated by conc. HCl to vomicine), was produced. The *methiodide*, m. p. 210° (decomp.), of (II) is converted by AgOH into the quaternary hydroxide; evaporation of a solution causes elimination of MeOH and a *betaine*, $C_{25}H_{32}O_5N_2$, m. p. 195—198° [*methiodide*, m. p. 245—250° (decomp.)], of (I) results. (II) is reduced catalytically (PtO_2) in AcOH to a *dihydro*-derivative, m. p. 183—185°. Successive treatment of didehydrovomicine with MeOH–KOH and MeI in H_2 gives the Me_2 ester (*dihydrochloride*, not melted at 320°) of an *acid*, $C_{46}H_{52}O_{10}N_4$, decomp. about 290°.

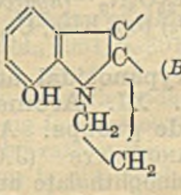
The compound previously described (*loc. cit.*) as the Bz derivative hydrochloride of vomicine [*benzylidene* derivative, m. p. 280° (decomp.)] is probably an additive compound, since it is hydrolysed immediately by dil. alkali to BzOH and vomicine. A similar *compound*, decomp. 185°, is obtained from BzCl and dihydrovomicine. Vomicinic acid contains an $\vdots NH$ group, since it gives a N-*nitroso*-derivative, decomp. about 190°.

VIII. Electrolytic reduction of vomicine affords *vomicidine*, $C_{22}H_{26}O_3N_2$, m. p. 283—284° (decomp.), which is sol. in alkali hydroxides (not in Na_2CO_3); the *Bz* derivative, m. p. 208—209°, is insol. in alkalis. The results so far obtained indicate that vomicine contains the (partial) structure (*A*),; vomicidine is represented by (*B*). The formation of *O*-Me derivatives (Part VII) involves fission of the oxazoline ring also.

(*A*.)



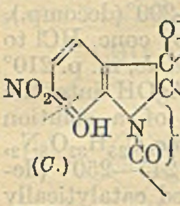
(*B*.)



IX. The acid, $C_{17}H_{22}O_5N_2$ ($+3H_2O$), $[\alpha]_D^{19}$ −90·6° in H_2O, previously obtained (*loc. cit.*) by oxidising vomicine, decomposes at 307—310° forming a *base* (IV), $C_{16}H_{22}O_3N_2$ (+EtOH), m. p. 302—310° (decomp.) according to the rate of heating, $[\alpha]_D^{17}$ −86·2° in H_2O, and is reduced catalytically (PtO_2) in H_2O to a mixture of an *acid* (V), $C_{17}H_{24}O_5N_2$ ($+4H_2O$), m. p. 264° (decomp.), and a *base* (VI), $C_{16}H_{26}O_2N_2$, m. p. 201—202°, $[\alpha]_D^{14}$ about +18° in EtOH (*Bz* derivative, m. p. 158° becoming red; *methiodide*, decomp. 295° after sintering at 124° and partial decomp. at 240—

250°). Similar reduction of (IV) gives (VI) and a small amount of a *base*, $C_{16}H_{24}O_3N_2$, m. p. 272° (decomp.) after sintering, also formed when (V) is heated. The acid, $C_{17}H_{22}O_7N_2$, previously described (*loc. cit.*), is probably $C_{18}H_{24}O_7N_2$, m. p. 266—268° decomp.).

Oxidation of dihydrovomicine with CrO_3 in dil. H_2SO_4 at 0°—room temp. gives (V) and an *acid*, $C_{18}H_{26}O_7N_2$ (+H_2O), m. p. 315° (decomp.) (darkens at 270°), which could not be reduced and is stable to acid $KMnO_4$. Partial formulæ are given for the above acids and their mode of formation is discussed in conjunction with the corresponding acids from strychnine.


(C.)

X. Vomicine and 20% HNO_3 at room temp. give a small amount of the *nitrate* (+$2H_2O$), darkens gradually above 200°, of *nitrovomicine* (as *C*), m. p. 253° (decomp.); the nitration conditions are difficult to reproduce. More dil. HNO_3 converts vomicine, after some months, into a *substance*, $C_{16}H_{20}O_9N_2$. Nitration with HNO_3 (*d* 1·4) and conc. H_2SO_4 gives a *compound* (VII), $C_{22}H_{23}O_9N_3$, red and orange-yellow forms, oxidised by Br in 48% HBr to a base, $C_{18}H_{22}O_5N_2Br_2$ [*hydrobromide*, reduced (Pd–$BaSO_4$) to a *hydrobromide*, $C_{18}H_{23}O_4N_2Br,HBr$]. (VII) probably results by further nitration of nitrovomicine and subsequent fission of the ring (with loss of NO_2) at the dotted line (in *C*). Dihydrovomicine and dil. HNO_3 give the *nitrate* (+$2H_2O$) of a *dinitrodihydrovomicine* (VIII), reduced by $SnCl_2$ and conc. HCl to an aminohydroxydihydrovomicine [*dihydrochloride*, not melted at 300° (darkens at 200°)]. The replacement of NO_2 by OH probably occurs by hydrolysis of an intermediate quinonoid oxime or imine. (VIII) is oxidised by Br in aq. HBr to the *compound*, $C_{15}H_{18}O_7N_2,HBr$ (+$3H_2O$). Nitration of dihydrovomicine with HNO_3 +H_2SO_4 gives a *compound* (IX), $C_{22}H_{24}O_{10}N_4$ (+H_2O), not melted at 300° (darkens from 200°), which is probably formed by fission of the ring (as above) and conversion of the *tert.*-OH into ·O·NO. (IX) is oxidised by Br in aq. HBr to the substance, $C_{19}H_{25}O_8N_3$ [*hydrobromide*, reduced catalytically (PtO_2) to a base, $C_{19}H_{29}O_5N_3$ (*dihydrochloride*)].

H. BURTON.

Trypanocidal action and chemical constitution. XI. Aromatic arsinic acids containing amide groups. A. COHEN, H. KING, and W. I. STRANGEWAYS (J.C.S., 1931, 3236—3257).—Me 4-arsinophthalate and aq. NH_3 at below 0°—room temp. give usually *5-arsinophthalamic acid* (I), shrinks 220—225° [*NH_4* salt (+$0·5H_2O$)], but in two cases *phthalamide-4-arsinic acid* (II) (+$1·5H_2O$), decomp. 147°, was obtained. (I) passes at 230°/vac. into *phthalimide-4-arsinic acid*, not melted at 300°, converted by aq. NH_3 at 50° into (I) and (II) and at 150° into (I). (I) and alkaline NaOBr give an acid *K* salt, $C_8H_7O_8As,C_8H_6O_8AsK$, of *3-hydroxy-5-arsinophthalic acid*, probably formed through an intermediate Br-acid. *p*-Xylylarsinic acid, m. p. 191—192° (decomp.) (lit. 223°), from *p*-xylidine, is oxidised by alkaline $KMnO_4$ to *2-arsinoterephthalic acid* (III), reduced (SO_2) to *terephthalic acid 2-arsenoxide* and converted by successive treatment with PCl_5 and $2N$-NH_3 into a mixture of chloroterephthalamide, 3 : 4-dichlorobenzamide, and *2-arsinoterephthalamic acid* (IV), not melted at 300°. Successive treatment of (III) with MeOH–HCl and $NaHCO_3$ gives *Me arseniterephthalate*, oxidised by H_2O_2 in aq. $NaHCO_3$ to *Me arsinoterephthalate* (V) and some 4-*Me* 1-*H* ester [converted by aq. NH_3 into (IV)]. (V) and aq. NH_3 afford 80% of *terephthalamidearsinic acid* and 20% of (IV). The 2-NO_2-derivative of *p*-tolylarsinic acid (convenient prep. given) is oxidised by $KMnO_4$ to 3-nitro-4-benzarsinic acid (acid *K* salt, $C_7H_6O_7NAs,C_7H_5O_7NAsK$), reduced by $FeCl_2$ and alkali to *4-arsinoanthranilic acid* (VI). (VI) is reduced by H_3PO_2 to *4-arsenoanthranilic acid* and converted by Ac_2O in *N*-NaOH into *acetic 4-arsino-N-acetanthranilic anhydride*, hydrolysed by short treatment with boiling $2N$-NaOH to *4-arsino-N-acetanthranilic acid hydrate*. *Acetanthranilic acid 4-arsenoxide* and *4-arsenoacetanthranilic acid* are prepared by the usual methods. Successive treatment of *anthranilic acid 4-dichloroarsine hydrochloride* with MeOH–HCl and $NaHCO_3$ gives *Me anthranilate 4-arsenoxide*, oxidised by alkaline H_2O_2 to *Me 4-arsinoanthranilate*, converted by aq. NH_3 into *anthranilamide-4-arsinic acid* (N-*Ac* derivative). (VI) is converted through its diazonium H sulphate into *4-arsinosalicylic acid*; the Me ester and aq. NH_3 give *salicylamide-4-arsinic acid.*

5-Nitroacetanthranilic acid (obtained with the 3-NO_2-isomeride from acetanthranilic acid and fuming HNO_3) is reduced by $FeSO_4$ and aq. NH_3 to 5-aminoacetanthranilic acid (*sulphate*; *hydrochloride*), convertible (Bart reaction) into 5-arsinoacetanthranilic acid (+H_2O) (VII), m. p. 236—237° (decomp.) (lit. 230°). (VII) and 5-arsinoanthranilic acid (VIII) are reduced by H_3PO_2 to 5 : 5′-*arsenoacet-*, not melted at 300°, and 5 : 5′-*arseno-anthranilic acids*, darkens and shrinks at about 280°, respectively. Attempted esterification of (VIII) or *anthranilic acid 5-dichloroarsine hydrochloride* (IX) with MeOH–HCl gives Me anthranilate, whilst successive treatment of (IX) with $SOCl_2$ and aq. NH_3 affords 5-chloroanthranilamide. The *Me* ester, not melted at 300°, of (VII), prepared by the Ag salt method, is convertible by aq. NH_3 into *acetanthranilamide-5-arsinic acid*. Hippuric acid *p*-arsenoxide (corresponding *dichloride*) is converted through Me *p*-arsinohippurate into *hippuramide-p-arsinic acid*, which is inferior in its therapeutic activity to the corresponding ethylamide.

The therapeutic activities of the above compounds are recorded and it is again found (cf. A., 1930, 796) that only the amides (or imides) possess curative action; several of the arseno-derivatives show some activity. In the last case, the solubilising action of the CO_2H group is more than counterbalanced by the physical properties of the As:As linking. The view that trypanocidal action is favoured when an arsenoxide is retained by the body is supported by the observations that the liver and spleen of mice contain more As 14 days after injection of salvarsan than they do 24 hr. after injection of 3-amino-4-hydroxyphenylarsinic acid.

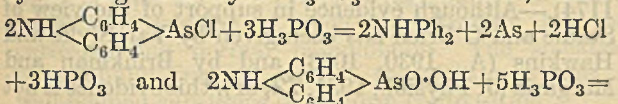
H. BURTON.

Absorption spectra of organic compounds of the salvarsan group. J. EISENBRAND (Arch. Pharm., 1931, 269, 683—689).—The absorption of

4-hydroxy-3-aminophenylarsinoxide, arsenobenzene, and salvarsan in the ultra-violet region is recorded. There is no relation between this absorption and the toxicity of the substances. Any relation would be expected in the visible region. R. S. CAHN.

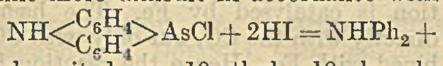
10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. XVII. Constitution of the nitro-derivatives produced from 3-nitrodiphenylamine-6′-arsinic acid and its homologues. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1931, 3270—3273).—2-*Bromo*-4-*nitrophenylarsinic acid* (I) (from 2-bromo-4-nitroaniline) has decomp. 240—242° (*Na* salt). With NH_2Ph (K_2CO_3; Cu; EtOH) it gives 3-*nitrodiphenylamine*-6-*arsinic acid*, decomp. 193° (shrinks at 135°), converted by SO_2 in aq.-EtOH–HCl into orange 10-*chloro*-3-*nitro*-5 : 10-*dihydrophenarsazine*, decomp. 268—271°, not identical with the red compound obtained by reducing 3-nitrodiphenylamine-6′-arsinic acid, which must therefore be the 1-NO_2-compound as previously suggested (A., 1927, 1210). Condensation of (I) with the appropriate amine affords 3′-nitro-4-, decomp. 194°, -3-, decomp. 116°, and -2-, decomp. 127—132°, -*methyldiphenylamine*-6′-*arsinic acid*, similarly converted into 10-*chloro*-7-*nitro*-2-, decomp. 263° (converted by H_2O_2 in AcOH into 7-*nitro*-2-*methylphenarsazinic acid*, not melting at 285°), -1(or 3)-, decomp. 292—294°, and -4-, decomp. 305—307°, -*methyl*-5 : 10-*dihydrophenarsazine*. J. W. BAKER.

Fission of the heterocyclic ring of dihydrophenarsazine derivatives with separation of arsenic. G. A. RAZUBAIEV (Ber., 1931, 64, [*B*], 2860—2863).—Separation of As from derivatives of 5 : 10-dihydrophenarsazine (with the exception of 10-aryl or -alkyl compounds) usually is smoothly effected by heating with cryst. H_3PO_3 at 120—180°, thus :



$$2NH{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}AsCl+3H_3PO_3=2NHPh_2+2As+2HCl+3HPO_3 \quad \text{and} \quad 2NH{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}AsO{\cdot}OH+5H_3PO_3=2NHPh_2+2As+4H_2O+5HPO_3.$$

Examples cited are 10-chloro-, 10-chloro-2 : 8-dinitro-, 10-chloro-5-aceto-, 5 : 4-benzo-10-chloro-5 : 10-dihydrophenarsazine, and phenarsazinic acid. With 10-alkyl (aryl) compounds at 200°, complicated decomp. results in the evolution of spontaneously inflammable derivatives of As and P. Diphenylenechloroarsine, chlorophenoxazine, and 3 : 10-dichloro-5 : 10-dihydroarsanthrene do not behave similarly. With aq. HI fission of the 10-alkyl derivatives is easier, but that of 10-chloro-5 : 10-dihydrophenarsazine more difficult in accordance with the scheme



$$NH{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}AsCl+2HI=NHPh_2+AsClI_2.$$

Examples cited are 10-ethyl-, 10-phenyl-, and 10-chloro-5 : 10-dihydrophenarsazine. H. WREN.

[Path to optically active germanium compounds.] E. KRAUSE (Ber., 1931, 64, [*B*], 2935).—The probable analogy between compounds of Ge and Pb is indicated (cf. Schwarz and Lewinsohn, A., 1931, 1435). H. WREN.

Salts of the tolyl- and mixed phenyltolyl-selenonium hydroxides. H. M. LEICESTER and F. W. BERGSTROM (J. Amer. Chem. Soc., 1931, 53, 4428—4436; cf. A., 1930, 231).—*Diphenyl*-p-*tolylselenonium chloride* (I), hygroscopic glass, resulted from $SePh_2Cl_2$, PhMe, and $AlCl_3$, from $Ph(p\text{-}MeC_6H_4)SeCl_2$, C_6H_6, and $AlCl_3$, and also from $SePh_2Cl_2$ and $(p\text{-}MeC_6H_4)_2Hg$ by heating until fusion begins. (I) and NaI give the corresponding *iodide*, decomp. 199—200° (all m. p. are corr.), which, when distilled, affords PhI and $p\text{-}MeC_6H_4{\cdot}SePh$, the dibromide of which has m. p. 128—129°; $p\text{-}IC_6H_4Me$ and $SePh_2$ could not be identified. $Se(p\text{-}MeC_6H_4)_2$ is best prepared from $p\text{-}MeC_6H_4{\cdot}N_2Cl$ and SeK_2; its *dichloride* decomp. 188—189°, with C_6H_6 and $AlCl_3$ yields *phenyldi*-p-*tolylselenonium chloride* (+$2H_2O$), m. p. about 130°, (+H_2O), decomp. 189—190°; the corresponding *iodide*, decomp. 189—191°, when heated, gives PhI and $Se(p\text{-}MeC_6H_4)_2$; the *picrate* has m. p. 158—159°. $(p\text{-}MeC_6H_4)_2SeCl_2$ and $HgPh_2$, on fusion, give $(p\text{-}MeC_6H_4)_2PhSeCl$ as the main product, but some $SePh_3Cl$ also results; this result indicates that the *p*-tolyl group is more negative than the Ph. $(p\text{-}MeC_6H_4)_2SeCl_2$ with PhMe and $AlCl_3$ or with $(p\text{-}MeC_6H_4)_2Hg$ gives *tri*-p-*tolylselenonium chloride* (+H_2O), decomp. 158—160°; the *iodide* (+H_2O), decomp. 202—203°, on dry distillation gives $p\text{-}IC_6H_4Me$ and $Se(p\text{-}MeC_6H_4)_2$. The *dichloride*, decomp. 149—150°, of *di*-m-*tolyl selenide*, b. p. 187—188°/16 mm., and Hg di-*m*-tolyl give the *compound*, $C_{21}H_{21}SeCl,HgCl_2$, m. p. 145°; removal of Hg from this with H_2S or NaOH and reaction with NaI gives *tri*-m-*tolylselenonium iodide*, decomp. 156—157°. $SePh_3OH$ was prepared in dil. solution; on concn. it decomposes to C_6H_6(?) and $SePh_2O$. Preliminary conductivity measurements indicate that the triarylselenonium iodides are weak electrolytes and approach the max. conductivity only at very high dilutions. The corresponding hydroxides are much better conductors. C. J. WEST (*b*).

Denaturation of proteins. XI. Effect of hydrogen-ion concentration on rate of denaturation of egg-albumin by carbamide. H. WU and E. F. YANG. **XII. Effect of denaturation and coagulation on titration curve of egg-albumin.** H. WU, S. C. LIU, and C. Y. CHOU. **XIII. Theory of denaturation.** H. WU (Chinese J. Physiol., 1931, 5, 301—308, 309—320, 321—344).—XI. At const. p_H, the rate of denaturation of egg-albumin by carbamide in aq. solution decreases with increasing ionic strength. At approx. const. ionic strength, the rate is min. at p_H 7·6. The p_H of neutral solution is displaced to 7·5±0·1, and the isoelectric point of egg-albumin from p_H 4·8 to 5·2 by carbamide. The rate of denaturation is therefore at a min. at the neutral point.

XII. Quinhydrone and hydrogen electrode titration curves of egg-albumin denatured in aq. solution at 70° are displaced to the alkaline side of neutrality as compared with curves for the natural protein. The change in acid- and base-binding power is confirmed by the increase in p_H of egg-albumin solution denatured by carbamide to exclude coagulation. Contrary to Booth (A., 1931, 316), the p_H of hæmoglobin solution increases on denaturation by EtOH.

XIII. A hypothesis is advanced to account for the above results. A. COHEN.

Determination of polypeptides in protein solutions. N. Fiessinger and M. Herbain (Compt. rend. Soc. Biol., 1930, **103**, 1211—1212; Chem. Zentr., 1931, ii, 95).—Polypeptides are determined from the difference between the N content of the filtrate from $CCl_3{\cdot}CO_2H$ and that of the filtrate from tungstate. In dil. solutions high vals. are obtained, particularly with serum. A. A. Eldridge.

Electrometric titration of proteins. J. Errera (Compt. rend., 1931, **193**, 1347—1350).—Titration curves (Sb electrode) for NaCl solutions of pea-nut globulin against 0·01*N*- and 0·02*N*-HCl are given. The isoelectric point is approx. p_H 4·7, whilst $K_a = 7{\cdot}1\times10^{-6}$ and $K_b = 1{\cdot}6\times10^{-10}$. Titrations of serum and of egg-white with different concns. of HCl confirm the stoicheiometric combination of protein with acids. Treatment of egg-white with NaOH at p_H 10·25—11·3 effects partial hydrolysis.

F. O. Howitt.

Composition of soya-bean protein. 1. Butyl alcohol extraction method. 2. Ester method. M. Mashino (J. Soc. Chem. Ind. Japan, 1931, **34**, 433B, 433—434B).—(1) [With S. Nishimura.] Fat-free soya-bean, purified with MeOH, was decomposed by 25% H_2SO_4; tyrosine crystallised from the neutralised conc. product. Extraction of the filtrate by BuOH yielded arginine, histidine, and lysine; leucine and phenylalanine were separated from the sol. part, and proline from the insol. part of the BuOH extract. Dibasic NH_2-acids were not extracted by BuOH. Omission of the MeOH purification prevented the extraction and crystallisation of the components.

(2) [With T. Shishido.] On evaporation of the Et_2O solution of the Me esters of the NH_2-acids from purified soya-bean protein a cryst. (monoclinic) *substance*, $C_{10}H_{16}O_8$, m. p. 78° (sol. in H_2O, Et_2O, MeOH, C_6H_6; insol. in light petroleum), was obtained. The glutamic acid isolated had $[\alpha]_D$ $+12{\cdot}4°$. Valine, leucine, proline, and phenylalanine were isolated by the ester method. E. Lewkowitsch.

Sensitive reaction of bivalent Fe, Co, Ni, and Cu. Determination of phenanthrene in commercial anthracene. T. Pavolini (Ind. Chim., 1930, **5**, 862—864; Chem. Zentr., 1931, ii, 283).—$Fe^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, and $Cu^{\cdot\cdot}$ give coloured ppts. (bluish-green, scarlet, ochre-yellow, chestnut-brown) with phenanthrenequinoneoxime. The tervalent cations do not react in this way. For the determination excess of the precipitant must be avoided and the ppt. must be washed on the filter with 40% EtOH.

A. A. Eldridge.

Determination of cysteine in proteins. S. L. Tompsett.—See this vol., 206.

Naphtharesorcinol reaction of alduronic acids. C. Neuberg and M. Kobel.—See this vol., 206.

Biochemistry.

Catalase as an agent for economising oxygen consumption. A. Staffe (Biochem. Z., 1931, **243**, 380—385).—Since blood is richer in catalase at high altitudes than at low and since the catalase content of cows' milk increases when they are taken to such altitudes, when they climb, or when they are exposed to the cold, it is concluded that catalase acts as an agent for economising O_2 consumption.

W. McCartney.

Segloff's method for the detection of blood. P. Schugt (Pharm. Presse, 1930, 166—167; Chem. Zentr., 1931, ii, 283).—The material (fæcal extract or urine, 1 c.c.) is preferably treated with 8 drops of AcOH and an equal quantity of H_2O_2 and then (without mixing) with a 5% solution of pyramidone in abs. EtOH. A violet ring indicates the presence of blood.

A. A. Eldridge.

Pipette for the handling of whole blood samples, for use with the Van Slyke gasometric apparatus. G. M. Guest (J. Biol. Chem., 1931, **94**, 507—509).—A pipette made from a 2-way stopcock and fitted with one bulb to contain and another to deliver the sample (1 c.c.) is described.

F. O. Howitt.

Clinical hæmoglobinometry. H. E. Harvey, V. H. Traxler, and R. L. Wright (J. Lab. Clin. Med., 1931, **16**, 1012—1016).—The Sahli double-standard hæmoglobinometer is preferred. Normal blood contains 14 mg. of hæmoglobin per 100 c.c.

Chemical Abstracts.

State of carbon dioxide in blood. O. M. Henriques (Biochem. Z., 1931, **243**, 241—255; cf. A., 1931, 1174).—Although evidence in support of the view of Stadie and O'Brien has been given by Van Slyke and Hawkins (A., 1930, 1053) and by Brinkman and Margaria (J. Physiol., 1931, **72**, 6P), this evidence is not satisfactory and evidence against the view has been adduced by the author and by others. On the other hand, whilst there is no evidence against the author's view, there is much to support it. W. McCartney.

Conversion of carbon monoxide into dioxide by green and mixed hæmins. E. Negelein (Biochem. Z., 1931, **243**, 386—395).—Provided that the amount of O_2 present is insufficient to oxidise all the Fe–CO compound, the conversion of CO into CO_2 by unreduced green or mixed hæmin in alkaline solution is catalysed by Fe. The hæmins react, not directly with the CO, but only with CO which is combined with Fe. Hence the reaction begins with the production of a little Fe–CO compound, a small amount of $Fe^{\cdot\cdot\cdot}$ of the hæmin being reduced. During the process the one Fe compound activates the O_2, the other the CO. It is not impossible that Fe–CO compound is also directly oxidised.

W. McCartney.

Decomposition of glucose in the blood. E. Sato (Nagoya J. Med. Sci., 1931, **5**, 167—174).—The decomp. of sugar in human blood is greatest in the first 3 hr., and decreases gradually up to 48 hr. No differences were observed at room temp. and 37°. The rates of decomp. by human blood-corpuscles in physiological salt solution and in blood-serum are almost the same, but decomp. is more rapid in phosphate solution. The decomp. decreases in proportion to hæmolysis. CHEMICAL ABSTRACTS.

Determination of galactose in blood and urine. V. J. HARDING and G. A. GRANT (J. Biol. Chem., 1931, 94, 529—539).—Ordinary baker's yeast grown in a medium containing galactose provides a strain capable of quantitatively removing galactose from aq. solutions or suitably treated physiological fluids. Galactose is not detectable by such yeast in fasting blood or urine either in normal subjects, in cases of late pregnancy, or 3 days *post partum*. The non-fermentable sugar of fasting urine in late pregnancy or the puerperium yields on hydrolysis " fermentable sugar " and " galactose sugar " in a ratio of approx. 2 : 1, a result inconsistent with the lactosuria of pregnancy or of lactation being produced by simple excretion of lactose in the urine. F. O. HOWITT.

Fœtal blood. II. Lactic acid content of umbilical cord blood under various conditions. N. J. EASTMAN and C. M. MCLANE (Bull. Johns Hopkins Hosp., 1931, 48, 261—268).—The fœtal blood-lactic acid is normal, but in infants at birth it is high (35 mg. per 100 c.c.); in asphyxiated infants it reaches 90 mg. CHEMICAL ABSTRACTS.

Colloidal chemical differences between paraglobulins of normal and antitoxic sera. P. VON MUTZENBECHER (Biochem. Z., 1931, 243, 100—112).—Using an improved method of electrodialysis, the paraglobulins of serum in diphtheria, tetanus, dysentery, and scarlet fever are found to sensitise Fe_2O_3 sol more feebly than the corresponding paraglobulin of normal serum. On the other hand, by fractional pptn. of diphtheritic serum, a paraglobulin is obtained which sensitises the sol much more strongly than the corresponding normal paraglobulin. The so-called paraglobulin fraction cannot therefore represent a well-defined substance of uniform composition.
P. W. CLUTTERBUCK.

Influence of hydrogen-ion concentration on sensitisation and protective action. P. VON MUTZENBECHER (Biochem. Z., 1931, 243, 113—124).—Electrodialysed paraglobulin coagulates Fe_2O_3 sol, and addition of acid, alkali, or neutral salts stabilises it. The action of HCl on the coagulation val. is followed, p_H measurements being given. Both the concn. and the protein charge as determined by the p_H affect the coagulation val. of protein–Fe_2O_3 sol mixtures.
P. W. CLUTTERBUCK.

Clinical determination of serum-proteins. E. H. FISHBERG and B. T. DOLIN (J. Lab. Clin. Med., 1931, 16, 1107—1112).—The protein content of blood sera or exudates is determined by colorimetric or electrometric measurement of the buffering power.
CHEMICAL ABSTRACTS.

Determination of fibrin, globulin, and albumin in blood-plasma. H. THEORELL and G. WIDSTRÖM (Z. ges. exp. Med., 1931, 75, 692—698; Chem. Zentr., 1931, i, 3706).—For 0·5 or 1 c.c. of plasma, N is determined micro-chemically in citrated plasma after combustion with H_2SO_4, in fibrin after recalcification and expression of the coagulum, in albumin after salting out the globulin with $MgSO_4$; globulin is determined by difference. A. A. ELDRIDGE.

Determination of amino-acids in blood-serum. K. L. ZIRM and J. BENEDICT (Biochem. Z., 1931, 243, 312—315).—The method of Linderstrøm-Lang (A., 1928, 536, 551) has been applied to the determination of NH_2-acids in blood-serum and can be used for other body-fluids also. The insolubility of pentamethoxytriphenylcarbinol is a disadvantage and α-naphthol-red gives equally good results. W. MCCARTNEY.

Effect of intravenous administration of pancreatic lipase on the blood-lipase. J. BALÓ and E. BACH (Z. ges. exp. Med., 1931, 75, 583—589; Chem. Zentr., 1931, ii, 69).—After a single administration (5 units) the blood-lipase is sharply increased, but becomes normal after 1 hr. After 25 injections in 32 days no effect on the blood-lipase was observed.
A. A. ELDRIDGE.

Calcium content of the blood of sea fish. M. FONTAINE and P. PORTER (Compt. rend., 1931, 193, 1218—1220).—Ca is distributed between the corpuscles and the serum of fish-blood in the same order and ratio as in men. No difference was discernible between the blood-Ca of Selachii and Teleostei or between male and female specimens.
C. C. N. VASS.

Two factors influencing serum-calcium and -inorganic phosphate of the rabbit. I. Influence of diet. II. Diurnal variation. E. F. DUPRÉ and E. SEMENOFF (J. Biol. Chem., 1931, 94, 341—351).—Dietary factors are mainly responsible for the wide variations in the serum-Ca and -inorg. P of normal rabbits. High vals. of the former are accompanied by low vals. for the latter, and *vice versa*. The high Ca and low P resulting from a diet of cabbage are respectively lowered and raised when cabbage is replaced by bran and oats. Normal vals. are established by fasting 12—24 hr. The normal serum-Ca increases by 1·0—1·5 mg. per 100 c.c. from morning to evening, whilst the inorg. P decreases by a similar amount. A. COHEN.

Copper content of blood. L. SCHINDEL (Klin. Woch., 1931, 10, 743—744; Chem. Zentr., 1931, ii, 76).—The Cu content of the corpuscles is always less than that of the plasma except for newly-born infants, for which the reverse holds. A. A. ELDRIDGE.

Specificity of hæmoglobin precipitins. L. HEKTOEN and A. K. BOOR (J. Infect. Dis., 1931, 49, 29—36).—Extraspecific action of antihæmoglobin precipitin may be overcome by diluting the serum.
CHEMICAL ABSTRACTS.

Specificity of serological reactions with simple chemical compounds (inhibition reactions). K. LANDSTEINER and J. VAN DER SCHEER (J. Exp. Med., 1931, 54, 295—305).—The specificity of inhibitory reactions involving substituted aromatic acids is influenced by the position of the substituent. Results of differentiation are given for antigens from 93 org. acids with immune sera. CHEMICAL ABSTRACTS.

Antigenic properties of fibrinogens. P. KYES and R. T. PORTER (J. Immunol., 1931, 20, 85—88).—Fowl, sheep, and horse fibrinogens, when injected into rabbits, produce antibodies sp. for the fibrinogen injected. CHEMICAL ABSTRACTS.

Cold hæmotoxin in heated serum. I. K. TOSHIMA (J. Biochem., Japan, 1931, 13, 291—308).—When heated for 30 min. at 75—90° the serum from rabbits immunised against human or chicken erythrocytes hæmolyses the erythrocytes at low temp. but does not affect them at 37°, and no complement is necessary for this purpose. The factor is present in the albumin fraction. CHEMICAL ABSTRACTS.

Specific combination in immunity reactions. J. R. MARRACK and F. C. SMITH (Nature, 1931, 128, 1077).—The sp. combination of haptene, *i.e.*, a compound of known composition, with antibody has been demonstrated. L. S. THEOBALD.

Factors influencing the concentration of complement in the blood. T. W. B. OSBORN (Biochem. J., 1931, 25, 2136—2149).—Young weaned rats tend to have a lower complement than adult animals. The ingestion of food may cause a variation in the blood-complement of rats. Irradiation of rats with a Hg-vapour lamp sometimes causes a rise in complement. Complement tends to be lower when the animals are fed on a diet deficient in vitamin-*A* than in the blood of controls receiving cod-liver oil. S. S. ZILVA.

Absorption spectrum of cytochrome. H. KATAGIRI and K. MASUDA (Mem. Coll. Agric. Kyoto, 1931, No. 15, 19 pp.).—Cytochrome from the thoracic muscle of the honey bee and other sources shows absorption bands at 605 (I), 566 (II), 550 (III), 539 (IV), 532 (V), 522 (VI), and 509 mμ (VII). When heated to 65° (I) is replaced by an asymmetrical band at 590 mμ. Heating to 45° in the presence of KCN destroys (II) and part of (V), new bands appearing at 575 and 539 mμ. The latter two bands are given by a substance (*A*) which is changed to *B* with absorption at 560 and 528 mμ by reduction at p_H 9·0. The change is reversed by neutralisation to p_H 5·5. Cytochrome *b* shows characteristic bands at 566 and 532 mμ. The *c* component, extracted from muscles or yeast by NaCl solution, shows seven bands at 667, 550, 539·5, 529·7, 521·8, 509, and 405—410 mμ, which on oxidation give place to bands at 563·7, 519—535, and 485 mμ. A. COHEN.

Suprarenal gland. E. C. KENDALL (Proc. Staff Meetings Mayo Clinic, 1931, 6, 296).—Separation of cryst. hexuronic acid, cryst. adrenaline, and the active agent of the cortex has been accomplished. CHEMICAL ABSTRACTS.

Structure of glutathione and the behaviour of the free compound and of derivatives towards enzymes. E. ABDERHALDEN and W. GEIDEL (Fermentforsch., 1931, 13, 97—114).—Glutathione (I) forms the following derivatives: *phenylcarbimido-* (II), m. p. 210° (decomp.) (giving *glutamic acid phenylhydantoin*, m. p. 143°, on acid hydrolysis); *α-naphthylcarbimido-* (giving *glutamic acid α-naphthylhydantoin* on acid hydrolysis); dl-*leucyl-* (oxidised form) [from dl-*α-bromo*iso*hexoyl-* (III), m. p. about 90° (decomp.)]; dl-*leucyl-* (cystine compound); *glycyl*-dl-*leucyl-* (from *chloroacetyl*-dl-*leucyl-*). Boiling (I) with H_2O gives cysteinylglycine, isolated as the *phenylcarbimido*-derivative (IV), m. p. about 150° (decomp.). *dl*-Leucyl-*dl*-leucylglycine ester hydrochloride with $CH_2Ph{\cdot}NH_2$ yields the -benzylamine, which when coupled with a carbimide gives *phenylcarbimido*-dl-*leucyl*-dl-*leucylglycylbenzylamine*. Hydrolysis with HCl gives *leucine phenylhydantoin*, m. p. 126°. Glycylbenzylamine was isolated as the *phenylcarbimido*-derivative, m. p. 202°. The benzylamine compound of glutathione could not be obtained. Cysteine Me ester hydrochloride, m. p. 131° (1 mol.), and $COMe_2$ (1 mol.) give an additive *compound*, m. p. 162°. Some polypeptides containing cysteine were synthesised: dl-*α-bromo*iso*hexoylcysteine Me ester*, *hippurylcysteine Me ester*, S-*benzyl*-n-*hippurylcysteine Me ester* (V).

Erepsin attacked neither (I) nor its derivatives. At p_H 7·8, HBr was eliminated from (III). Trypsin-kinase hydrolysed the oxidised (I), yielding glycine, but not the reduced form. It also attacked (II), (III), and (IV), but not (V). Cathepsin had no action on (I) or its derivatives, but (I) accelerates its action on gelatin. (I) was not hydrolysed by pancreas powder or yeast maceration juice. J. H. BIRKINSHAW.

Spermine in human tissues. G. A. HARRISON (Biochem. J., 1931, 25, 1885—1892).—The distribution of the base in human tissues is virtually the same as that found by Dudley and Rosenheim (A., 1926, 194). It occurs in human fæces. The spermine content of the human prostate is remarkably high. The absence of spermine from bull's semen is possibly due to the absence of a true functional prostate in that animal. A modification has been introduced in the steam-distillation method (A., 1924, i, 294) to obtain the base as phosphate more readily in a relatively pure state. S. S. ZILVA.

Histological detection of uric acid and urates. A. SCHULTZ and W. SCHMIDT (Arch. path. Anat. Physiol., 1931, 280, 529—533; Chem. Zentr., 1931, ii, 96).—Uric acid (but not urate) is detected by means of hæmatoxylin-carmine or methylene-blue and picric acid. By a modification of technique Na urate may be detected. A. A. ELDRIDGE.

Basic amino-acids of wool. A. M. STEWART and C. RIMINGTON (Biochem. J., 1931, 25, 2189—2192).—Australian wool contained 0·55% of histidine, 6% of arginine, and 2·2% of lysine (cf. A., 1929, 632; 1930, 1328). S. S. ZILVA.

Constitution of the keratin molecule. J. B. SPEAKMAN and M. C. HIRST (Nature, 1931, 128, 1073—1074).—From a study of the action of acids on wool it is concluded that one of the linkings between the peptide chains in the keratin mol. is a salt of glutamic acid and arginine; the former may be replaced occasionally by aspartic acid and the latter by lysine. L. S. THEOBALD.

Fatty acids from oil of cantharis (*Mylabris pustulata*, Fb., India). B. H. IYER and P. R. AYYAR (J. Indian Inst. Sci., 1931, 14A, 40—45).—From the EtOAc extract of the dried beetles, 12·5% of crude fat was obtained by extraction with (40—60°) petrol. It consisted of 5% of unsaponifiable matter, 11% of palmitic acid, 27% of stearic acid, 46% of oleic acid and isomeride, 1% of arachidic acid, with 10% of dissolved cantharidin. C. C. N. VASS.

Fatty acids and cholesterol in the seminal vesicles of the guinea-pig. S. Comhaire (Arch. Biol., 1931, **41**, 485—490).—The cholesterol content of the epithelium of the seminal vesicles of the guinea-pig is approx. const.; the fatty acid content increases and the unsaponifiable matter decreases with advancing stages of sexual development.

A. G. Pollard.

Determination of the iodine value of lipins. M. Yasuda (J. Biol. Chem., 1931, **94**, 401—409).—The Hanus method gives very high results for the I val. of cholesterol and its esters. For lipins generally, the Rosenmund–Kuhnhenn method, employing pyridine dibromide as halogenator, is preferable. Details are given for the adaptation of this method to the micro-determination of the I val. of tissue extracts, in conjunction with Bloor's micro-determination of lipins. A. Cohen.

Histochemistry of phenols and their derivatives. L. Lison (Arch. Biol., 1931, **41**, 343—436).—Diazo-reactions are utilised in technique developed for the examination of phenols and derivatives in animal tissues. A. G. Pollard.

Calcium salts of bone. L. J. Bogert and A. B. Hastings (J. Biol. Chem., 1931, **94**, 473—481).—The inner and outer portions of bone and also the cortex were analysed before and after treatment by various methods for removal of org. matter. The inner and outer parts do not differ materially in inorg. constituents, which are more conc. in the cortex. Normal methods of ashing result in loss of carbonates. The chief constituent is probably a cryst. salt, $CaCO_3,2Ca_3(PO_4)_2$. F. O. Howitt.

Dehydrating agents for paraffin embedding. L. A. Margolena (Stain Tech., 1932, **7**, 25).—$Bu^{\alpha}OH$ is recommended. H. W. Dudley.

Determination of total protein in cerebrospinal fluid. J. B. McNaught (J. Lab. Clin. Med., 1931, **16**, 999—1012).—Tsuchiya's reagent is employed, the ppt. being measured volumetrically, after centrifuging, in a calibrated tube. Normal vals. are 17—40 (average 29) mg. per 100 c.c.

Chemical Abstracts.

Determination of total precipitable protein in cerebrospinal fluid. A. R. Bauer and P. H. Schenck (J. Lab. Clin. Med., 1931, **16**, 1090—1100).—The ppt. produced by a reagent containing 1·5% of picric acid and 3·0% of citric acid is centrifuged in a calibrated tube. Chemical Abstracts.

Indoxyl (indican) in the milk of the cow and the goat. C. Hervieux (Compt. rend., 1931, **193**, 1480—1482).—Small amounts of indican were present in all normal milks examined. W. O. Kermack.

Influence of environmental temperature on the percentage of butter-fat in cow's milk. H. J. Brooks (J. Dairy Sci., 1931, **14**, 483—493).—The % of fat in butter is inversely related to environmental temp. The latter factor exerts a greater influence on the fat content of milk than does the stage of lactation. A. G. Pollard.

Colorimetric determination of the thiocyanate content of gastric juice. G. Lockemann and W. Ulrich (Biochem. Z., 1931, **243**, 150—159).—A method is described for the colorimetric determination of CNS′ in gastric juice with the help of the $FeCl_3$ reaction which permits the detection of CNS′ in dilutions of 1 in 10^6 corresponding with a content of 0·1 mg. per 100 c.c. P. W. Clutterbuck.

Stimulating effect of amino-acid hydrochlorides on gastric secretion. I. Experiments on men. II. Experiments on dogs with gastric pouches. III. Experiments on men in whom the substances are introduced into the duodenum. J. Tagawa (Biochem. Z., 1931, **243**, 330—343, 344—354, 355—368).—I. Although neither NH_2-acids (glycine, *l*-leucine, *l*-phenylalanine, *l*-tyrosine, *l*-asparagine, *d*-glutamic acid, *d*- and *l*-histidine, *l*-cystine, *d*-alanine, *l*-tryptophan) nor HCl have appreciable effect on gastric secretion the hydrochlorides of the acids stimulate secretion to varying extents and at various rates. Of the acids tested glutamic is the most active. It is probable that the stimulating effect produced by proteins takes place only after degradation to NH_2-acids and combination of these with HCl.

II. In dogs with gastric pouches the administration of the NH_2-acid hydrochlorides has effects very similar to those produced in man. The effect produced by glutamic acid hydrochloride is not influenced by administration of atropine, is inhibited by administration of adrenaline, and slightly increased by administration of pilocarpine.

III. When the acids are introduced into the human duodenum they have no effect on the gastric secretion, but introduction of HCl or of the hydrochlorides of the acids has stimulating effects similar to those produced by introduction of the hydrochlorides into the stomach. In all cases glutamic acid hydrochloride is the most active compound. No connexion can be traced between the extent of the stimulating effect and the $[H^{\cdot}]$ of the solutions given. It is concluded that the NH_2-acid hydrochlorides exert their stimulating action after resorption below the duodenum.

W. McCartney.

Variations in pancreatic secretion during hyperglycæmia resulting from intravenous injection of glucose. J. La Barre and P. Destrée (Compt. rend. Soc. Biol., 1930, **105**, 35—36; Chem. Zentr., 1931, ii, 76).—Hyperglycæmia stimulates the higher nervous system, leading to vigorous pancreatic secretion. A. A. Eldridge.

Fluorescence of pigments of urobilin group. Fluorescence spectra. C. Dhéré and J. Roche (Bull. Soc. Chim. biol., 1931, **13**, 987—1014).—The fluorescence of mesobiliviolin, mesobilirubinogen, and preps. of urobilin and hydrobilirubin in EtOH solution alone and in presence of Zn and Hg salts is described. The absorption and fluorescence spectra under these conditions are depicted.

H. A. Piggott.

Relation between endogenous and enterotropic uric acid. H. Rothmann (Ver. deut. Ges. inn. Med., 1930, **42**, 159 pp.; Chem. Zentr., 1931, ii, 78).—Adenosinephosphoric acid is excreted with the bile into the intestine, and is therefore a source of enterotropic uric acid. A. A. Eldridge.

Detection of formaldehyde in urine. E. Chierici (L'Ateneo Parm., 1930, 2, No. 1; Chem. Zentr., 1931, ii, 95—96).—Labat's reaction is employed. A. A. Eldridge.

Colour reaction for carbohydrates. Detection of hexoses and pentoses in urine. E. Chierici (L'Ateneo Parm., 1930, No. 2, 8 pp.; Chem. Zentr., 1931, ii, 96).—Urine (0·2 c.c.) is added without mixing to H_2SO_4 (4 c.c.); after careful mixing 5% alcoholic gallic acid (0·2 c.c.) is added. In the cold or on gentle warming (H_2O-bath) a green coloration indicates hexoses or carbohydrates yielding hexoses with H_2SO_4. If the reaction is not given, but the deproteinised urine reduces Fehling's solution, pentose is present. A. A. Eldridge.

Occurrence of phenol derivatives in urine. Determination by means of the Millon reaction. O. Fürth and R. Scholl (Biochem. Z., 1931, 243, 274—291).—The phenolic compounds in urine not volatile in steam can be separated into an Et_2O-sol. (substances derived from tyrosine) and an Et_2O-insol. fraction. The amount of phenolic substances in urine cannot be determined by direct application of the Millon reaction, but the amount of these fractions can be colorimetrically determined with the Millon reagent if the urine is treated in the manner described. The usual methods for the determination of the indican content of urine are very inaccurate, but by using Na indigotinsulphonate for colorometric comparison estimates of this content can be made. Normal human urine contains traces only of Et_2O-insol. phenolic substances, but has an average of 4·7 mg. per 100 c.c. of the Et_2O-sol. (as tyrosine) and 0·8—1·3 mg. per 100 c.c. of indigo (from indican). No relationship can be found between the indican (derived from putrefaction of protein) content of urine and its content of Et_2O-insol. phenolic compounds. In diseases in which the function of the liver is seriously affected, in advanced tuberculosis, and to some extent in other diseases also, the content of Et_2O-insol. phenolic compounds increases greatly, although the content of the Et_2O-sol. fraction does not alter. In dementia præcox and in amentia increase in the amount of phenolic compounds in the urine occurs only exceptionally. In the rabbit, dog, and guinea-pig poisoning with P leads to great increase in the amount of Et_2O-insol. phenolic compounds in the urine. W. McCartney.

Urinary proteases. I. B. H. E. Cadness and C. G. L. Wolf (Fermentforsch., 1931, 13, 1—21).—Ninhydrin-positive, dialysable substances are present in most pregnancy and pathological urines, but absent from normal urines. Certain pathological urines contained enzymes which digested placental tissue slightly. The enzyme of pregnancy urine was not sp. for placenta, but digested other substrates. The $COMe_2$ ppt. of all urines examined hydrolysed fibrin. Boiling the $COMe_2$ ppt. for 2 min. prevented the attack on placenta, and autoclaving for 30 min. the attack on fibrin. J. H. Birkinshaw.

Pigment metabolism and destruction of blood in pernicious anæmia. R. F. Farquharson, H. Borsook, and A. M. Goulding (Arch. Int. Med., 1931, 48, 1156—1185).—In severe relapses and, to a smaller extent, in patients without much anæmia the fæcal excretion of urobilinogen increases to several times the normal val. Serum-bilirubin also increases, and in some cases urobilin is found in the urine. Normal vals. are rapidly restored during the reticulocyte response following effective treatment with liver or liver extract. The pigment excretion is attributed to early destruction of the abnormal red blood-cells of anæmia. Liver therapy favours the production of red cells which are less readily destroyed, and the blood returns to normal. A. Cohen.

Relationship between oxygen consumption and nitrogen metabolism. I. Pernicious anæmia. C. W. Baldridge and A. Baker (J. Clin. Invest., 1931, 10, 529—543).—There is a direct causal relationship between the increase in N catabolism and increased O consumption and also between N storage and decrease in O requirement. Chemical Abstracts.

Crystalline derivative of an acid present in liver. Correction. R. West and M. Howe (J. Biol. Chem., 1931, 94, 611).—The statement that the cryst. quinine salt previously described (A., 1930, 1309) is clinically active is now withdrawn. Contrary to previous findings (*loc. cit.*), an appreciable amount of active material is removed by BuOH from liver extract saturated with picric acid. The active material is recovered from the BuOH extract by shaking with dil. mineral acid. H. Burton.

Iron and carbon of visceral pigments. J. Paviot, R. Chevallier, and A. Badinand (Compt. rend. Soc. Biol., 1930, 105, 18—19; Chem. Zentr., 1931, i, 3708).—Anthracotic lungs contain an Fe-bearing pigment, generally in quantity exceeding that of C. The intensity of the colour depends on the condition of the Fe and not on its quantity. Pb could not be found in the lungs of a worker in a lead mine. The Fe content of the spleen is lower than that of the lungs or liver. A. A. Eldridge.

Potassium content of bone marrow in carcinoma. T. Hoffmann (Biochem. Z., 1931, 243, 145—149).—Human bone marrow has during growth a high K content, but in adults decreases to $\frac{1}{4}$—$\frac{1}{5}$ of this val. In presence of carcinoma, K enrichment of bone marrow again occurs, the vals. being at least double those of normal adults. The Na content showed similar but not such regular variations, whilst the Ca content was irregular and could not be correlated with growth. P. W. Clutterbuck.

Lipins of human tumours, especially the sulphophospholipins of the tumours. A. Bolaffi (Atti R. Accad. Lincei, 1931, [vi], 14, 62—64).—Various neoplastic tissues, human and otherwise, all exhibit distinct analogies as regards their lipoidal constitution. Each contains a complex sulphophospholipin extractable by hydrated $COMe_2$ (*d* 0·850), but, if pure, insol. in anhyd. $COMe_2$. This lipin, which is moderately conc. in the tumours, appears to have a constitutional character sp. for each tumour and is characteristic if not absolutely sp. for neoplastic tissue. In human tumours it is probably identical with jecorin. T. H. Pope.

Determination of small amounts of phosphatides and cholesterol in tissues. M. Jowett and E. W. Lawson (Biochem. J., 1931, **25**, 1981—1990).—The phosphatides are pptd. with $MgCl_2$ and the P not pptd. is subtracted from the total P. The cholesterol is pptd. with digitonin and determined gravimetrically. S. S. Zilva.

Phosphatide and cholesterol contents of normal and malignant human tissues. M. Jowett (Biochem. J., 1931, **25**, 1991—1998).—Pure malignant tissues have a higher phosphatide and cholesterol content and tend to show a higher phosphatide–cholesterol ratio than do malignant tissues admixed with normal tissue. Malignant tissues show a high proportion of bound cholesterol. Malignant and benign tumours show a higher phosphatide : cholesterol ratio than do the neighbouring tissues from which they may have arisen. S. S. Zilva.

Kidney threshold for glucose in diabetic and non-diabetic persons. B. V. Glassberg (J. Lab. Clin. Med., 1931, **16**, 948—952).—The kidney threshold varies greatly. Neither glycosuria nor the presence of both glycosuria and a high blood-sugar level necessarily indicates a disturbance in carbohydrate metabolism. Chemical Abstracts.

Mineral metabolism during involution of simple goitre. E. J. Baumann, S. Kurland, and N. Metzger (J. Biol. Chem., 1931, **94**, 383—391).—Rabbits suffering from thyroid deficiency caused by a diet of cabbage retain Ca, Mg, and P, whilst the metabolism of Na, K, Cl, and S is unaffected. Administration of I to such rabbits increases the excretion and restores the balance of Ca, Mg, and P. A. Cohen.

Change in the isoelectric point of the hæmoglobin and of the chlorine distribution in the blood in exophthalmic goitre. J. Glass (Z. klin. Med., 1931, **116**, 478—509; Chem. Zentr., 1931, ii, 260).—Normally the isoelectric point of the oxyhæmoglobin is between 5·95 and 6·40 (average 6·20); in exophthalmic goitre it is usually higher. In exophthalmic goitre and on administration of thyroxine the Cl distribution in the blood is acidotic in character. A. A. Eldridge.

Acid–base equilibrium in pathological conditions. II. Alkalosis observed in hypertensive states. E. Muntwyler, C. T. Way, and D. Binns (J. Clin. Invest., 1931, **10**, 489—506).—In 6 of 12 cases of persistent hypertension with slight N retention a plasma-HCO_3' val. above 0·031 equiv. was found; in 11 cases the plasma p_H exceeded 7·48. Two cases with vomiting showed loss of Cl′ and total base and a rise in HCO_3'. Chemical Abstracts.

Thiosulphate treatment of pellagra. I. Sabry (J. Egypt. Med. Assoc., 1931, **14**, 603—610).—Intravenous injection of 10 c.c. of 10% $Na_2S_2O_3$, repeated 20—60 times according to the severity of the disease, supplemented by a milk diet, is an effective treatment for pellagra. A. Lawson.

Iron in normal and pathological tissues and its biological interpretation. IV. Iron content of various organs of white rats during pregnancy and under normal conditions. V. Rice pigeons. VI. Starvation rabbits. VII. Rachitic rabbits. K. Kojima (Nagoya J. Med. Sci., 1931, **5**, 78—82, 83—93, 94—102, 103—109).—IV. In all organs studied, except the uterus, where it was increased, the Fe content of pregnant rats was less than that of normal females.

V. Pigeons fed on polished rice showed increase in the Fe content of the liver and spleen, and the Fe content of the brain and peripheral nerve was greater than in starvation pigeons. The Fe content of various grains, and of polished and unpolished rice, is parallel with the vitamin-*B* content. All preps. of vitamin-*B* examined contained Fe, although in small amount. Vitamin-*A* preps. contained only traces or none.

VI. The Fe content of the liver increased with duration of the starvation period, but the spleen-Fe decreased.

VII. In rachitic rabbits the spleen- and liver-Fe decreases, but the blood- and bone marrow-Fe increases. In the bones there is no difference between rachitic and normal rabbits. Chemical Abstracts.

Nitrogen, calcium, and phosphorus balances in late gestation under a specified dietary regime. I. G. Macy, E. Donelson, M. L. Long, A. Graham, M. E. Sweeny, and M. M. Shaw (J. Amer. Dietet. Assoc., 1931, **6**, 314—320).—During the 7th and 8th months of pregnancy, N, Ca, and P were stored on an adequate diet. Chemical Abstracts.

Healing of rickets coincident with low serum-inorganic phosphorus. G. Stearns and J. D. Boyd (J. Clin. Invest., 1931, **10**, 591—602).—In two children with a persistent low level of serum-inorg. P clinical healing was observed with sufficient retention of Ca and P for building bone. Chemical Abstracts.

Viscosity of the blood-serum in syphilis. Serum-albumin and -globulin content. M. C. McIntyre (J. Lab. Clin. Med., 1931, **16**, 952—956).—Increased viscosity (1·82, 1·99) does not appear to be due only to an increase in serum-globulin. Chemical Abstracts.

Enzymes and immunity. M. Ghiron (Atti R. Accad. Lincei, 1931, [vi], **14**, 48—52).—Addition of an active, atoxic, sterile suspension in glycerol of a lipase from pig's liver to a broth culture of the tubercle bacillus results in an attenuated strain of the organism. When inoculated systematically into an animal during the development of the tubercular process, the enzymic suspension arrests the disease at the first phase of the inflammatory process, which may be followed by a cure. T. H. Pope.

Variations in the content of reduced glutathione in toxic and infected conditions. R. A. C. Gherzi (Anal. Asoc. Quím. Argentina, 1931, **19**, 173—197).—The liver of the guinea-pig contains more reduced glutathione than the heart and kidneys. The amounts in each organ are normally const., but poisoning by KCN, $HgCl_2$, As_2O_3, $CHCl_3$, $H_2C_2O_4$, strychnine, morphine, atropine, or snake-venom causes characteristic variations in the amounts present in different organs, generally independent of the size of the dose, but dependent in some cases on the mode of administration. Subcutaneous injections of carbuncle, tetanus, or Koch's bacilli, or of tetanus toxin, all cause a decrease in the reduced glutathione content of the liver and kidneys and an increase in that of the heart, but diphtheria toxin increases the amount in the liver. In anæmia produced by bleeding the ratio (red corpuscles)/(reduced glutathione content of blood) is decreased. Injection of thyroid extract increases the amount of reduced glutathione in the organs. R. K. Callow.

Energy changes in the anaërobic phosphagen synthesis in muscle extract. O. Meyerhof and K. Lohmann (Naturwiss., 1931, **19**, 575—576).—The energy required for phosphagen synthesis is covered approx. by the sum of the energies of decomp. of glycogen to lactic acid and of adenylpyrophosphate to inosic acid, NH_3, and phosphate. This explanation holds especially for cold-blooded muscles. With rabbit muscle complications arose through the secondary action of the adenylic acid compound, and agreement is not so good. J. W. Smith.

Behaviour of lactacidogen in fatigue induced by stimulation of isolated frog's gastrocnemius. D. Wilhelmi (Z. physiol. Chem., 1931, **203**, 34—47). —Fatigue of frog's gastrocnemius by isolated stimuli was studied in relation to lactacidogen content. The change in lactacidogen content depends on the season; in autumn, fatigue always causes an increase. During the last third of August, *R. esculenta* regularly and *R. temporaria* to some extent show a decrease. In the transition period the effect on lactacidogen content is variable even with *R. esculenta*. The seasonal change is about a month earlier for *R. temporaria* than for *R. esculenta*. J. H. Birkinshaw.

Fission of lactacidogen in muscular contraction. II. G. Embden and H. Jost (Z. physiol. Chem., 1931, **203**, 48—57; cf. Arch. Soz. Biol. de Montevideo, Suppl., Fasc. II, 1931).—Frog's gastrocnemii were electrically fatigued until immersion in liquid air produced no contraction. A muscle so fatigued and electrically stimulated to contraction at the moment of immersion usually contained much less lactacidogen than a fatigued muscle immersed without such treatment. J. H. Birkinshaw.

Heat production of skeletal muscle in arrested lactic acid formation. E. Fischer (Pflüger's Archiv, 1931, **226**, 500—517; Chem. Zentr., 1931, i, 3698—3699).—The quotient initial heat/(tension × length of muscle) is unchanged by poisoning with $CH_2Br·CO_2H$. The poisoned muscle shows under aërobic conditions the same heat production as a normal muscle under anaërobic conditions. A. A. Eldridge.

Oxidation of lactic acid by brain-tissue. C. A. Ashford and E. G. Holmes (Biochem. J., 1931, **25**, 2028—2049; cf. A., 1930, 1312).—A Meyerhof quotient can be obtained, but no carbohydrate synthesis takes place when brain-tissue is shaken with lactate in the presence of a hydrogen carbonate buffer in an O_2–CO_2 atm. The O_2 uptake is greater in the presence of a CO_2–hydrogen carbonate buffer than in the presence of phosphate and increases with increased O_2 tension in both cases. The R.Q. both of the brain-tissue alone and of the "extra O_2" are close to unity even in the case of animals rendered hypoglycæmic by insulin injection. Glucose, lactate, succinate, and glycerophosphate act with brain-tissue as H_2 donators to methylene-blue. Glycerol and dihydroxyacetone are without effect on the reduction time; formate, acetate, and mandelate prolong it. "Extra O_2" gives a true measure of lactic acid oxidised. Volatile acid or any substance capable of binding hydrogen sulphite is not formed from lactic acid in presence of brain-tissue. There is a small increase in inorg. and in total P at the expense of org. P both in presence and in absence of lactate. There is no synthesis of any P compound from the fraction of lactic acid which disappears and is not accounted for by oxidation. S. S. Zilva.

Importance of bile acids in carbohydrate metabolism. X. Influence of bile acids and phosphates on sugar assimilation. S. Fuzita (J. Biochem., Japan, 1931, **13**, 219—236).—The formation of glycogen in the rabbit's liver is stimulated by oral administration of Na_2HPO_4 (0·5 g. per kg.) or cholic acid. Glycogen formation from glucose, mannose, and galactose is, however, thereby diminished (except with glucose and very small quantities of Na_2HPO_4). Chemical Abstracts.

Action of adrenaline and the mechanism of glycogen mobilisation in the isolated frog's liver. E. Geiger (Biochem. Z., 1931, **243**, 160—174).—Perfusion of frog's liver with isotonic Ringer's solution is accompanied with absorption of H_2O by the liver. Addition of adrenaline to the perfusion fluid inhibits absorption of H_2O and leads to a loss of it by the liver. Adrenaline does not constrict the vessels of the perfused frog's liver and the loss cannot be explained in terms of vaso-constriction. The loss of H_2O is also obtained in glycogen-free livers of hibernating frogs and cannot be the result of decomp. of glycogen. It does not appear to be caused by alteration in permeability, but is most probably the result of contraction of cell-colloids, which can be inhibited by ergotamine. Histamine, which brings about mobilisation of glycogen, also leads to a loss of H_2O by the liver, a loss inhibited by ergotamine. $CaCl_2$ and Na_2SO_4 added to the Ringer's solution cause a mobilisation of glycogen and a loss of H_2O by the liver. A causal relationship exists between contraction of cell-colloids and glycogen mobilisation, the cell-enzyme system being brought into action by contraction. P. W. Clutterbuck.

Relationship of fat and carbohydrate degradation in the liver. Biological oxidation–reduction potentials. J. Kühnau (Biochem. Z., 1931, **243**, 14—50).—The oxidation–reduction potential and the glutathione content of the liver is followed with normal rabbits and rabbits in experimental ketosis. Both in phloridzin and P ketosis, the potential with max. excretion of ketone substances is considerably displaced to the positive side, the reduced and total glutathione contents are decreased, and the oxidised glutathione content is increased. After injection of dihydroxyacetone, the potential of the liver in phloridzin ketosis returns rapidly to negative vals., the total and reduced glutathione contents increase, but the abs. amount of oxidised glutathione decreases only slightly. The liver is therefore able to form reduced glutathione from an unknown precursor. In P ketosis, the potential and the total glutathione content of the liver are not affected by injection of dihydroxyacetone. The bearing of the results on fat and carbohydrate metabolism is discussed.

P. W. Clutterbuck.

Body-fats of the pig. I. Influence of ingested fat on the component fatty acids. R. Bhattacharya and T. P. Hilditch (Biochem. J., 1931, **25**, 1954—1964).—There is a general relationship of the various fatty acids of the pig body-fats to those of tallows (A., 1931, 757). The composition of the outer layer of back fat which is most unsaturated differs from that of the inner layer, the latter being intermediate in type between the former and the perinephric fat, which it resembles more closely. The differences are much reduced when the diet of the animals includes arachis oil. Body-fats from pigs which consume the relatively saturated shea butter are not greatly different from those of the animal fed on the control ration. The consumption of arachis oil leads to an increase of unsaturation in the stored fat and also increases the proportion of linoleic acid in the unsaturated acids. Much of the normal fat of the pig must be derived from carbohydrate or other non-fatty part of the ration. S. S. Zilva.

Do peanut- or arachis nut-fed hogs yield lards containing arachidic acid ? A. H. Gill and G. T. Vaala (Science, 1931, **74**, 548).—Saponification followed by methylation of lard obtained from hogs fed on peanuts gave no evidence of Me arachidate; palmitic and stearic acids only were indicated.

L. S. Theobald.

New contributions in sterol metabolism. R. Schoenheimer (Science, 1931, **74**, 579—584).—A lecture. L. S. Theobald.

Animal ergosterol synthesis. G. Bischoff (Klin. Woch., 1931, **10**, 455; Chem. Zentr., 1931, i, 2497).—During the hatching of hen's eggs the hydrogenated sterol constituent (dihydrocholesterol) increases from 3·2 to 9·1%. Contrary to Schönheimer, a simultaneous dehydrogenation of other sterol constituents was not observed. The ergosterol content in hen's eggs amounts to approx. 0·17% of the substances pptd. by digitonin. During hatching the total sterol increases to approx. 5%.

L. S. Theobald.

Urinary excretion of ketonic substances during starvation in various species of animals. E. F. Terroine and H. Trimbach (Compt. rend., 1931, **193**, 1345—1347).—A diminution in ketonuria occurs during starvation following a milk diet in the pig, rabbit, dog, cat, and rat. In the pig alone there is an increase in $COMe_2+CH_2Ac\cdot CO_2H$ during inanition, but this is more than compensated by the decrease in β-hydroxybutyric acid. No parallelism exists between the N-excretion and the ketonuria during the period of starvation. F. O. Howitt.

Parenteral denaturation of foreign proteins. V. Effect of starvation. T. H. Boone (J. Immunol., 1931, **21**, 139—140).

Chemical Abstracts.

Nutritive value for growing swine of the proteins of linseed meal and of cottonseed meal both alone and in combination with the proteins of maize. H. H. Mitchell (J. Agric. Res., 1931, **43**, 743—748).—The true digestibility of cottonseed proteins is 83%, that of linseed proteins 94%, and that of maize proteins 91%. The combinations of cottonseed and maize proteins and of linseed and maize proteins give average coeffs. of 86% and 92%, respectively. The biological vals. of all three proteins are almost identical at 61—63%. The pig appears to utilise maize proteins as efficiently as the rat, but cottonseed and linseed proteins less efficiently.

W. G. Eggleton.

Nitrogen balance in the white rat on a diet of ovalbumin and fat or of ovalbumin and carbohydrate. F. Maignon and M. A. Chahine (Compt. rend., 1931, **193**, 1474—1476).—White rats fed on a diet of ovalbumin supplemented by either fat or carbohydrate of approx. equal calorific val. show the smaller loss of N and better utilisation of the protein with the fat than with the carbohydrate when these are administered in relatively small quantities. With larger relative amounts of fat or carbohydrate, these may exert approx. equal effects or the carbohydrate may even be more active than the fat.

W. O. Kermack.

Rôle of non-essential amino-acids in partly covering the specific endogenous nitrogen loss. Mézincesco (Compt. rend., 1931, **193**, 1469—1471).—The administration of non-essential NH_2-acids (glycine, alanine, aspartic or glutamic acid) to pigs on a purely carbohydrate diet decreases the negative N balance, the extent of the decrease (25—30%) being of the same order as that obtained with NH_4 citrate. The effect of the acids appears therefore to depend solely on the NH_2-group as such. The administration of these acids is without definite effect on the excretion of total and neutral S or of creatinine. W. O. Kermack.

Amino-acid metabolism. I. Relative rates of amino-acid disappearance and urea formation. V. C. Kiech and J. M. Luck (J. Biol. Chem., 1931, **94**, 433—449).—NH_2-acid metabolism has been studied by analysis of whole bodies and excreta of rats. The high NH_2-N content of rats immediately after injection of *dl*-alanine soon decreases to the normal val., but only about 50% of the N is recovered as urea. Following injection of glycine and *l*-aspartic acid a 6—8 hr. lag in formation of urea is observed, which is followed by a period in which urea formation exceeds that possible from deamination. 3—4 hr. after injection of *l*-aspartic acid the decrease in NH_2-N is replaced by an increase, due to protein hydrolysis stimulated by the NH_2-acid. Glycine administered *per os* is metabolised without lag in urea formation, and no endogenous-protein hydrolysis occurs. The results are explained by the formation of intermediate N compounds. A. Cohen.

Behaviour of heterocyclic compounds in the frog. K. Kusui (J. Biochem., Japan, 1931, **13**, 343—350).—The frog excretes nicotinic acid partly unchanged. It converts to a slight extent ingested quinoline and *iso*quinoline into Me compounds, and

oxidises a small amount of 2-methylquinoline to quinaldinic acid. Quinoline-2-carboxylic acid behaves differently from picolinic acid in not being conjugated with glycine, but appearing in the urine largely unchanged. Although 2-dihydroxypropylquinoline is readily oxidised *in vitro* to quinaldinic acid, this transformation does not occur in the frog.
CHEMICAL ABSTRACTS.

Acid–base balance in animal nutrition. IV. Effect of long-continued ingestion of acid on reproduction in swine, rats, and rabbits. A. R. LAMB and J. M. EVVARD (J. Biol. Chem., 1931, 94, 415—422).—Three generations of swine were reared in 3·5 years on a normal diet to which were added 200—300 c.c. of N-H_2SO_4 daily without impairing growth, health, or reproductive ability. No abnormal composition of bone resulted. Similar results were obtained with rats receiving acid salts equiv. to 1·5—2·0 c.c. of N-acid daily. Rabbits reproduce successfully if the daily balance of acid received is not greater than 5 c.c. (N). Higher doses are fatal. The acid is mainly excreted as acid phosphate, the rabbit showing less ability than swine or rats to neutralise acid with NH_3. A. COHEN.

Magnesium absorption in dogs and its effect on the metabolism of calcium. H. G. BARBOUR and J. E. WINTER (J. Pharm. Exp. Ther., 1931, 43, 607—620).—The administration to dogs of equal quantities of Mg oxide, lactate, or gluconate produces apparently equal increases in the Mg content of the serum and has practically no effect on the Ca content. When account is taken of the Mg content of the three compounds, it follows that Mg gluconate is most readily absorbed and MgO least. When large doses of Mg lactate or gluconate are administered over a long period no loss of Ca occurs provided that the P_2O_5 intake is adequate. If the P_2O_5 intake exceeds 4 millimol. per kg. per day, extra Ca is retained.
W. O. KERMACK.

Calcium and phosphorus metabolism. XII. Effect of ingestion of acid-producing substances. R. F. FARQUHARSON, W. T. SALTER, D. M. TIBBETTS, and J. C. AUB. **XIII. Effect of ingestion of phosphates on the excretion of calcium.** R. F. FARQUHARSON, W. T. SALTER, and J. C. AUB. **XVIII. Temporary fluctuations in the level of calcium and inorganic phosphorus in blood-serum of normal individuals.** R. F. FARQUHARSON and D. M. TIBBETTS (J. Clin. Invest., 1931, 10, 221—249, 251—269, 271—286).—XII. Excretion of Ca varied with the total excess acid eliminated and especially with the output of NH_3. The quant. increase in Ca excretion from acid ingestion was influenced by the basal level of Ca excretion as well as by the amount of excess acid ingested. Alkali has little effect on Ca excretion. Fæcal Ca remained const. even with great changes in the acidity of the diet.

XIII. Great variation in P did not appreciably affect urinary or fæcal Ca. A high-protein diet, the acidosis being controlled by $NaHCO_3$, was without effect. NaH_2PO_4 produced a rise in urinary acidity, but had no effect on excretion of NH_3 or Ca.

XVIII. The normal fasting vals. of serum-Ca and -P change little over long periods. Large amounts of carbohydrates cause a fall in serum-inorg. P, and sometimes an increase in Ca.
CHEMICAL ABSTRACTS.

Effect of iodoprotein decomposition products on processes of development and regeneration. W. BRANDT, H. MATTIS, and E. NOLTE (Biochem. Z., 1931, 243, 369—379; cf. A., 1931, 1463).—Six fractions obtained by hydrolysis of the iodoprotein accelerate development of tadpoles and newts. The most active fraction produces metamorphosis in tadpoles in 8 days and in newts in 12—14 days, and in its action is exactly similar to active thyroid preps. The growth before metamorphosis and the intensity with which amputated parts are regenerated are not accelerated to the same extent as is metamorphosis itself. W. McCARTNEY.

Contraction of rectus abdominis muscle of frogs caused by acetylcholine. R. MIURA (Arch. exp. Path. Pharm., 1931, 163, 553—561).—Acetylcholine (1 : 50,000—100,000) induces a strong and persistent contraction in the rectus muscle, but has only a weak action in the sartorius; in no instance was there an increase in the lactic acid level. Higher concns. (1 : 1000) impair the excitability and increase the lactic acid content in both muscles to the same extent as occurs with tetanising stimulation, which also causes a marked decrease in phosphagen content, a phenomenon not exhibited by acetylcholine (1 : 50,000). Hence fundamental differences exist between contraction due to acetylcholine and that due to tetanisation. F. O. HOWITT.

Reflex-hyperlipæmia. Y. D. KOSKOFF and J. G. D. DE BARENNE (Science, 1931, 74, 550).—Reflex-hyperlipæmia generally occurs when the sciatic nerve of cats is electrically stimulated; the increase in blood-fat is abrupt, since it is present in the blood drawn immediately after afferent stimulation. L. S. THEOBALD.

Influence of denervation on sympathomimetic action. T. MASAYAMA (Arch. exp. Path. Pharm., 1931, 163, 562—582).—The changes in glycogen and phosphagen levels in the tibialis muscle of the rabbit were investigated during (*a*) denervation by section of the corresponding ischiadicus, (*b*) curarisation, (*c*) treatment with adrenaline, caffeine, and tetrahydro-β-naphthylamine before and after denervation, (*d*) treatment with adrenaline and caffeine in curarised muscle, and (*e*) administration of picrotoxin, ergotamine, and insulin in normal muscle. The results are discussed with reference to the nervous control of the "chemical tonus" of muscle. Thus the correlation existing between glycogen and phosphagen metabolism is dependent on that between the sympathetic and central motor nervous control. F. O. HOWITT.

Effect of naphthalene on the tissue oxidation of the lens [of the eye]. D. MICHAIL and P. VANCEA (Compt. rend. Soc. Biol., 1930, 105, 59—60; Chem. Zentr., 1931, ii, 83).

Appearance of a reducing substance in the urine after administration of ethyl urethane. E. ZUNZ (Arch. Int. Pharmacodyn. Ther., 1930, 38, 359—362; Chem. Zentr., 1931, ii, 261).—Different animal species react differently as regards the appearance of a reducing substance of unknown composition; also different samples of Et urethane differ in their power to generate the substance.

A. A. Eldridge.

Effect of narcosis on the blood-lactic acid. I. H. Schmidt and E. Schmutzler (Schmerz, Narkose, Anæsth., 1930, **3**, 309—325; Chem. Zentr., 1931, ii, 82).—With frog's muscle, Et_2O or $CHCl_3$ does not inhibit the resynthesis of lactic acid to hexosephosphoric acid, but rather promotes it. Clinical increase in blood-lactic acid is attributed to liver injury. After N_2O the increase in blood-lactic acid is less than after Et_2O.

A. A. Eldridge.

Lactic acid metabolism. I. Blood-lactic acid in narcosis. Pharmacology of "pernocton." F. Matakas (Arch. exp. Path Pharm., 1931, **163**, 493—504).—"Pernocton" injected into various species of animals results in unchanged levels of blood-lactic acid and -sugar, whilst Et_2O or urethane produces a rise. The increase in blood-lactic acid due to Et_2O narcosis is a secondary action due to inhibition of oxidation and increase in lactic acid formation by striated muscle and not to any influence on the respiratory centres.

F. O. Howitt.

Influence of narcotics on sugar-excretion threshold. Y. Iwanaga (J. Biochem., Japan, 1931, **13**, 351—368).—Morphine produces hyperglycæmia and glycosuria in the dog, lowering the sugar excretion threshold, but only when large doses are given. When the threshold is raised by adrenaline the effect of morphine is very marked. $CHCl_3$ and Et_2O narcosis produce hyperglycæmia and lower the sugar-excretion threshold, especially in dogs treated with adrenaline. EtOH does not affect the blood-sugar level, and lowers the sugar threshold less than other narcotics. Morphine, $CHCl_3$, and Et_2O markedly reduce the sugar threshold abnormally increased by acetylcholine.

Chemical Abstracts.

Action of some hypnotics on methylene-blue decolorisation. K. Behnecke (Arch. exp. Path. Pharm., 1931, **163**, 594—601).—Urethane, "voluntal," and "adalin" inhibit, whilst veronal accelerates the decolorisation of methylene-blue by muscle incubated in PO_4''' buffer with hexose- or glycerophosphoric or succinic acid as donator. Veronal, however, inhibits the O_2-consumption by such a system and hence behaves in a manner similar to that of PhMe or HCN.

F. O. Howitt.

New hypnotic, ethyl-β-ethylbutylbarbituric acid, and some derivatives of β-ethylbutyl alcohol. E. Fourneau and J. Matti.—See this vol., 142.

Hypnotic action of ethyl-β-ethylbutylbarbituric acid ("Fourneau 769") on the rat. D. Bovet (J. Pharm. Chim., 1931, [viii], **14**, 523—527).—The compound is 8·2 times as active as veronal on the rat, and dos. tol./dos. cur.=72/28; it is 3 times as active as veronal on mice.

R. S. Cahn.

Metabolic action of cutaneously applied camphor and related substances. M. Tennenbaum (Arch. exp. Path. Pharm., 1931, **163**, 505—516).—A decrease in blood-sugar level is produced in rabbits by inunction of olive oil solutions of camphor, turpentine oil, and to a smaller extent of borneol or menthol. The effect commences ½ hr. after treatment, reaches a max. in 5 hr., and then decreases. No correlation between chemical constitution of the compounds and hypoglycæmic action could be deduced.

F. O. Howitt.

Animal calorimetry. XLI. Influence of phloridzin glycosuria on the metabolism of dogs after thyroidectomy. M. Dann, W. H. Chambers, and G. Lusk [with J. Evenden] (J. Biol. Chem., 1931, **94**, 511—527).—Thyroidectomy in dogs tends to inhibit the increase in heat production and also in protein metabolism following administration of phloridzin. With one prep. of phloridzin the "extra sugar," which could be accounted for by the glycogen reserves and did not arise from metabolism of fat as indicated by the R.Q., was only gradually eliminated. In this instance the D : N ratios were high, whereas with another prep. of phloridzin the ratios were lower and the delayed elimination of extra glucose was not apparent.

F. O. Howitt.

Effect of cholic acid on excretion of creatinine under the influence of vegetative nervous system poisons. A. Taku (J. Biochem., Japan, 1931, **13**, 237—254).—Tetrahydro-β-naphthylamine, caffeine, atropine, and $CaCl_2$, but not pilocarpine, increase the creatinine excretion of the rabbit. The action is inhibited by simultaneous administration of cholic acid.

Chemical Abstracts.

Distribution of quinine in the organism. A. A. Kirstner and M. M. Pantschenkov (Arch. Schiffs- u. Tropen-Hyg., 1931, **35**, 286—297; Chem. Zentr., 1931, ii, 266).—In rabbits treated with quinine the highest concn. was present in the brain, followed by the lungs; moderate quantities were found in the liver, but relatively little in the blood and spleen. The quantity in human blood after 6 hr. was 1% of the dose. The max. quinine concn. is found after 3 hr.; the red corpuscles contain three times as much as the plasma.

A. A. Eldridge.

Colloid chemistry of the nervous systems. III. Histamine. W. D. Bancroft and J. E. Rutzler, jun. (J. Physical Chem., 1931, **35**, 3189—3206; cf. A., 1931, 1454).—The superior cervical ganglia of rabbits are peptised by NaCNS and reversibly agglomerated by histamine. In presence of lipins, histamine may appear to cause swelling of the nervous tissue, but is more probably being dissolved by the lipins. $CHCl_3$ dissolves in the lipins of the cerebral cortex, but does not peptise the proteins. *In vivo* ephedrine and NaCNS antagonise histamine. Pre-treatment with NaCNS counteracts skin reactions to histamine and giant-ragweed pollen extract. Reversible agglomeration of protein colloids is probably responsible for skin reactions, since histamine, $CaCl_2$, lactic acid, and morphine behave similarly.

C. T. Snell (*c*).

Reversible coagulation in living tissue. VIII. W. D. Bancroft and J. E. Rutzler, jun. (Proc. Nat. Acad. Sci., 1931, **17**, 597—601; cf. A., 1931, 1328).—Bulbocapnine is an agglomerating agent, as shown by an improvement after its administration in a case of human dementia præcox, and by its induction of catatonia and catalepsy in rabbits. In rabbits NaCNS and ephedrine sulphate relieve bulbocapnine catatonia on account of their peptising action, whilst Na amytal aggravates this condition on account of its agglomerating action. N. H. Hartshorne.

Reversible coagulation in living tissue. IX. W. D. Bancroft, R. S. Gutsell, and J. E. Rutzler, jun. (Proc. Nat. Acad. Sci., 1931, **17**, 637—642; cf. A., 1931, 513, 649, 872, 1088).—NaCNS by its peptising action of the tissue colloids coagulated by morphine addiction removes or alleviates the withdrawal symptoms when the drug is suddenly withdrawn from addicted dogs. The use of NaCNS for human addicts is advocated. F. O. Howitt.

Taste deficiency for creatine. R. J. Williams (Science, 1931, **74**, 597—598).—Creatine is tasteless to certain individuals. L. S. Theobald.

Curariform action of quaternary ammonium salts. H. R. Ing and W. M. Wright (Proc. Roy. Soc., 1931, **B**, **109**, 337—353).—The time of diffusion of quaternary NH_4 salts into isolated frogs' gastrocnemii is appreciable in comparison with the time of poisoning. In isolated sartorii the diffusion period is negligible. Methyl-, *n*-amyl-, hexyl-, heptyl-, and octyl-trimethylammonium iodides are equal in curariform action on the isolated sartorius. *n*-Propyl-, ethyl-, and dodecyl-trimethylammonium iodides are progressively less active. The $PhMe_3$, $PhCH_2PhMe_2$, and Me_4 derivatives are equally active. Replacement of Me by Et in the last-named lowers the activity rapidly, the $MeEt_3$ and Et_4 derivatives causing initial increases in the response of sartorii to indirect stimulation. Slight activity is shown by NMe_3 and NPhMeEt oxides. Paralysed sartorii recover slowly in NMe_4I solution. For the latter drug a temp. coeff. of 1·5 per 10° at 23·5—13·5° and 13·5—3·5° is found for the rate of poisoning. Curariform action may be due to ionic exchange of the permutit type between the drug and the affected muscle system. A. Cohen.

Effects on albino rats of nutrition solely with seeds of *Lathyrus sativus*, L. V. Zagami (Atti R. Accad. Lincei, 1931, [vi], **14**, 218—221).—These seeds form an incomplete or qualitatively deficient food for growing rats. Although nervous or motor phenomena related to those described as lathyrism are not observed, young rats fed solely on these seeds show diminished resistance, torpor, and slow growth, especially of the genital organs and skeleton. T. H. Pope.

Assimilation of aluminium by the human system. S. J. Lewis (Biochem. J., 1931, **25**, 2162—2167).—Normal blood usually contains no Al and when it does the proportion is very small. A considerable quantity of Al is found in the blood after one meal of food containing Al. Similar observations apply to milk. S. S. Zilva.

[Physiological] action of calcium. I. Effect of intravenous injections of calcium salts on the heart in cattle having diseased mineral metabolism. Dependence of action of calcium on the heart on mineral composition of the blood-serum. L. Seekles, B. Sjollema, and F. C. van der Kaay (Biochem. Z., 1931, **243**, 316—329; A., 1931, 383).—In parturient paresis and grass staggers in cattle injections of $CaCl_2$ produce fundamentally the same effects on the heart, viz., alterations in the frequency, which is sometimes greatly increased, with blocking, during and soon after the injection. The effect on the heart in parturient paresis is dependent on the mineral composition of the blood before injection; if the serum is low in Ca and high in P there is predisposition to dangerous changes in frequency, whilst, on the other hand, high Ca and low P lead to harmless changes. In grass staggers there is no connexion between the mineral composition of the blood and the effect of the injection; the effect of this composition on the heart in this disease is due to other influences and to greatly increased sensitivity. It is concluded that the occurrence of heart block and systolic arrest in parturient paresis could be prevented by injections of mixtures, in suitable proportion, of $CaCl_2$ and $MgCl_2$. W. McCartney.

Blood-calcium following intravenous injection of calcium salts. G. D. Greville (Biochem. J., 1931, **25**, 1931—1942).—The rate of fall of serum-Ca at any time greater than 5 min. after the intravenous injection of $CaCl_2$ and of Ca lævulate into cabbage-fed rabbits is approx. proportional to the excess at that time of the serum-Ca above the final const. level. There is a large disappearance of serum-Ca during the first 5 min. not accounted for by this relationship. Serum-Ca as determined by direct pptn. gives an accurate measure of the Ca content of the blood following the intravenous injection of Ca lævulate. S. S. Zilva.

Bismuth derivative of sodium β-hydroxy-γ-thiolpropanesulphonate. A. Leulier and M. Juvin (J. Pharm. Chim., 1931, [viii], **14**, 527—531).—The *Bi* salt of Na β-hydroxy-γ-thiolpropanesulphonate, injected into guinea-pigs, is excreted in the urine and fæces, but some is deposited in various organs, notably the liver and kidney. R. S. Cahn.

Toxicological practice. W. Austen (Pharm. Zentr., 1931, 72, 385—388).—In a case of Hg poisoning Hg was determined as HgS. On addition of Br water to the steam-distillate of portions of the intestine from a case of lysol poisoning a turbidity was obtained; none was obtained in the distillates from the kidney, urine, or liver. It was not possible to demonstrate the individuality of the Br ppt. In a case of As poisoning As was conc. in the stomach, but was present also in the intestines and the liver. C. C. N. Vass.

Hydrases. Mechanism of the action of and the specificity of fumarase. K. P. Jacobsohn (Biochem. Z., 1931, **243**, 1—13).—Fumarase does not add the elements of H_2O to methylfumaric acid. This is not due to toxicity, since when mixtures of methylfumaric and fumaric acids are used, the former is unaffected, whereas the latter is converted into *l*-malic acid. The mechanism of fumarase action is discussed. P. W. Clutterbuck.

Activation of oxido-reductions by cozymase. H. von Euler and R. Nilsson (Biochem. J., 1931, 25, 2168—2171).—Phosphate is not required for aldehyde transformation when catalysed by dialysed liver-juice and purified cozymase. The transformation in dialysed liver-juice is increased by the addition of hexosediphosphate or of phosphate. Both in the presence and in the absence of hexosediphosphate cozymase is indispensable for the transformation of MeCHO by liver-juice. S. S. Zilva.

Enzymic amylolysis. I. Capability for enzymic fission of amylo- and erythro-substances from starch. M. Samec and E. Waldschmidt-Leitz (Z. physiol. Chem., 1931, **203**, 16—33).—The action of pancreatic, malt-, and barley-amylases on amylo- and erythro-amyloses from potato-starch was compared. Amylo-amyloses are completely hydrolysed by all the enzymes, which differ, however, in their rate and manner of action as shown by the I colour reaction. In pancreatic fission of the erythro-amyloses a partial breakdown product remains which is resistant to further hydrolysis. J. H. Birkinshaw.

Influence of proteins and protein derivatives on the enzymic hydrolysis of starch by malt-diastase. B. Filipowicz (Biochem. J., 1931, **25**, 1874—1884).—EtOH retards at p_H 5·6 hydrolysis of starch or dextrin by malt-diastase to an extent proportional to the concn. of EtOH. The percentage of retardation is greater the more the p_H of the system exceeds 4·5, the optimal p_H in the presence or absence of EtOH. The activity of 20% EtOH amylase solutions is greater than that of similar solutions not containing EtOH after keeping up to 48 hr. Ovalbumin, gelatin, peptone, glycine, and aspartic acid retard at p_H below and accelerate at p_H higher than 4·5 to an extent increasing with the alkalinity of the medium. In the case of glycine the relative acceleration is greater the higher is the temp. Carboxylic acids and amines retard the reaction. S. S. Zilva.

Hydrolysis of concentrated sugar solutions by invertase. H. A. Auden and E. R. Dawson (Biochem. J., 1931, **25**, 1909—1916).—The rate of hydrolysis by invertase of solutions containing 40% or more of sucrose decreases as the substrate concn. increases, the relation between substrate concn. and invertase activity being linear. The optimum temp. for the hydrolysis of 70% sucrose in the presence of invertase is 65—70°. The relation between the crit. increment in g.-cal. per mol. and the temp. for the hydrolysis of 70% sucrose by invertase can be expressed by $E=20,500-168t$. S. S. Zilva.

Relationships between structure of saturated aliphatic alcohols and their inhibiting effect on liver-esterase. D. Glick and C. G. King (J. Biol. Chem., 1931, **94**, 497—505).—The inhibitions of sheep liver-esterase acting on Et butyrate by *n*-primary alcohols increase rapidly as the series is ascended. Those of the 7 isomerides of amyl alcohol decrease as the steric hindrance about the OH group increases. With secondary alcohols the effect of steric hindrance is eclipsed by that of the length of the hydrocarbon chain. Other aspects of the inhibitory power of these alcohols are discussed. F. O. Howitt.

Distribution of phosphatase in the tissues of teleosts and elasmobranchs. O. Bodansky, R. M. Bakwin, and H. Bakwin (J. Biol. Chem., 1931, **94**, 551—560).—Phosphatase occurs both in the cartilaginous skeleton of the elasmobranch and, to a greater extent, in the bony skeleton of the teleost. Hence an assumption of a necessary association between presence of the enzyme and the occurrence of ossification (cf. A., 1923, i, 730; 1925, i, 201; 1929, 1197; 1931, 258) is not justified. F. O. Howitt.

Does bodily effort give rise to defence enzymes specific for substrates prepared from incretion organs? S. Buadze (Fermentforsch., 1931, **13**, 126—127).—Severe exercise produced no effect. J. H. Birkinshaw.

Latent period in autolysis. A. Neuberger and H. Reinwein (Biochem. Z., 1931, **243**, 225—235).—By addition of phosphate, pyrophosphate, hexosediphosphate, and lactate to rats' liver-pulp, autolysis sets in immediately, hexosediphosphate having the strongest action. NaCl, KCl, NaF, and Na_2SO_4 have no effect on the latent period. Acetate, citrate, and glycerophosphate have slight and irregular accelerating action. Adjusting the p_H of the autolysate to 5 also causes autolysis to set in immediately. P. W. Clutterbuck.

Latent period of autolysis with [tissues of] fasting animals. A. Neuberger (Biochem. Z., 1931, **243**, 236—240).—With liver of fasting animals, the latent period is usually shorter, and addition of acetate and citrate accelerates the autolytic process more strongly than with normal tissue. Phosphate addition accelerates autolysis as in the experiments with normal animals. P. W. Clutterbuck.

Enzymic synthesis of proteins with special reference to the action of pepsin. D. P. Cuthbertson and S. L. Tompsett (Biochem. J., 1931, **25**, 2004—2013).—The optimum $[H^{\cdot}]$ for the synthesis of plastein from conc. digests of egg- and serum-albumin and from caseinogen incubated at 37° is p_H 4. The formation from the first two sources increases with rise of temp., reaching a max. at 70°. Increase in the concn. of enzyme increases plastein formation in conc. peptic digests of egg- and serum-albumin. The ratio of the decrease in the NH_2 and CO_2H groups in the process of formation from egg- and serum-albumin and caseinogen is 1 : 1. There is no appreciable liberation of NH_3. The longer a protein is allowed to digest the less is the yield. Better yields are obtained from egg- and serum-albumin than from caseinogen. Plastein is not obtained from the products of digestion of gelatin. S. S. Zilva.

Nature of proteases. X. Determination of the optimum temperature for the digestion of egg-albumin by frog-pepsin at p_H 1·6—1·9. N. P. Piatnitzki (Z. physiol. Chem., 1931, **203**, 10—15; cf. A., 1931, 1191).—The activity of frog's gastric juice increases with rising temp. to a max. at 45—50°; it is destroyed when the juice is heated to 65° for ½ hr. Frog and human pepsins show no substantial differences in behaviour. J. H. Birkinshaw.

Nature of proteases. X. Relations between activity of pepsin preparations and viscosity of the digestion mixtures. I. A. Smorodincev and A. N. Adova (Fermentforsch., 1931, **13**, 36—46; cf. A., 1931, 1191).—The changes in viscosity of gelatin solutions under the action of pepsin at 38° reach a limit in 3 hr. The fall in viscosity indicates the strength of the prep. In digestion of caseinogen, active preps. are distinguished by the fact that the viscosity rises gradually to a max. in 3 hr. The viscosity of 1% enzyme solutions is independent of the activity. J. H. Birkinshaw.

Homogeneity of trypsin solutions prepared by the method of Waldschmidt-Leitz. II. E. Abderhalden and E. von Ehrenwall (Fermentforsch., 1931, **13**, 47—51; cf. A., 1931, 766).—A trypsin solution originally inactive to *dl*-leucylglycine developed ereptic power after contact with glycerol at 37°. After removal of erepsin by adsorption on $Al(OH)_3$ C_γ, ereptic power again developed. After repeating the adsorption, no ereptic action was observed on keeping, but it was evoked by the addition of glycine. J. H. Birkinshaw.

Behaviour of polypeptides composed of *l*(+)-alanine towards dilute alkali and enzymes. E. Abderhalden and W. Gohdes (Fermentforsch., 1931, **13**, 52—63).—The following polypeptides (and precursors) were obtained from *l*(+)-alanine etc. and *d*(+)-α-bromopropionyl chloride [from *d*(−)-alanine, $[\alpha]_D^{20}$ −14·1° (d-*methylenecamphor*-d-*alanine Et ester*, m. p. 108—109°, $[\alpha]_D^{22}$ +250°)]; l-*alanyl*-l-*alanine*, m. p. 297° (decomp.), $[\alpha]_D^{20}$ −21·6°; *di*-l-*alanyl*-l-*alanine* (+½H_2O), decomp. 250—253°, $[\alpha]_D^{18}$ −72·2° (*Br*-precursor, decomp. 193—195°, $[\alpha]_D^{20}$ −47·2° in *N*-NaOH); *tri*-l-*alanyl*-l-*alanine* (+H_2O), decomp. 269—272°, $[\alpha]_D^{22}$ −120·5° (*Br*-precursor, decomp. 243—245°); *tetra*-l-*alanyl*-l-*alanine* (+H_2O), decomp. above 275°, $[\alpha]_D^{19}$ −136·4° (*Br*-precursor, decomp. 260—261°); *penta*-l-*alanyl*-l-*alanine* (+H_2O), colloidal, decomp. above 278° (*Br*-precursor, decomp. 269—272°). *N*-NaOH hydrolysed the polypeptides more rapidly as mol. wt. increased. Gastric juice did not attack any of the polypeptides, trypsin-kinase hydrolysed the tetrapeptide most readily, and also attacked the penta- but not the di-peptide. Erepsin attacked all the polypeptides. J. H. Birkinshaw.

Behaviour of hydroxyacylamino-acids or polypeptides towards enzymes. E. Abderhalden and F. Schweitzer (Fermentforsch., 1931, **13**, 128—136).—By boiling the corresponding Br-compounds with H_2O and pyridine the following were prepared: dl-α-*hydroxy*iso*hexoylglycine*, m. p. 108—109°, dl-α-*hydroxy*iso*hexoylglycylglycine*, dl-α-*hydroxy*iso*hexoyl*-dl-*leucylglycylglycine*, m. p. about 140°. α-Bromoacetyl-*dl*-leucine gave the *betaine anhydride* of *acetyl*-dl-*leucylpyridonium hydroxide*, m. p. 223—224°, and with NMe_3 the corresponding *trimethylammonium hydroxide* derivative, m. p. 236—237° [additive *compound* with acetyl-*dl*-leucinetrimethylammonium bromide (1 mol.), m. p. 222°]. *dl*-α-Bromo*iso*hexoylglycyl-*dl*-leucine gave the *betaine anhydride* of iso*hexoylglycyl*-dl-*leucinepyridonium hydroxide*, m. p. 206° (decomp.). J. H. Birkinshaw.

Alcoholic fermentation. S. Veibel (Dansk Tidsskr. Farm., 1931, 5, 201—218; cf. A., 1931, 1332).—Neuberg's theory of the production of EtOH by fermentation from hexoses is discussed. A mixture of sugar, NaH_2PO_4, and $NaHCO_3$ in H_2O was fermented for periods of 4, 8, and 32 hr. After 4 hr. the salt produced is nearly pure hexosemonophosphate, whilst the 8-hr. salt contains 35% and the 32-hr. salt contains 45% of trehalosemonophosphate. The ratio of diphosphate to glucosephosphate increased continuously during the experiment, reaching a val. of 8·7 after 32 hr. The percentages of P present at the close of the 4-, 8-, and 32-hr. periods in combination as inorg. P, trehalosemonophosphate, glucose- and fructose-mono- and -di-phosphate have been determined, and the bearing of the results on the mechanism of phosphorylation is discussed. H. F. Harwood.

Acetoacetic acid and yeast. E. Friedmann (Biochem. Z., 1931, **243**, 125—144).—The material extracted by Et_2O from a solution obtained in yeast fermentations in presence of $CH_2Ac{\cdot}CO_2H$, on methylation with diazomethane and fractionation of the esters, consists of a small fraction, b. p. 40—44°/9 mm., comprising a mixture of the esters of *dl*- and *d*(−)-lactic acid together with a chief fraction, b. p. 64—68·5°/11 mm., which is Me *d*(+)-β-hydroxybutyrate. The same products are obtained with yeast and $CH_2Ac{\cdot}CO_2H$ in the absence of sugar. The two samples of Me β-hydroxybutyrate had $[\alpha]_D$ +25·48° and +17·12°, respectively, differing amounts of the *dl*-ester being also present. In fermentations in presence of sugar, the yield of β-hydroxybutyric acid from the rotation is 38% and of ester isolated from 86 to 100% of the $CH_2Ac{\cdot}CO_2H$ added, the difference representing the *dl*-variety. In absence of sugar, the yield of β-hydroxybutyric acid from the rotation is 13 to 17% and from isolation 95% of the $CH_2Ac{\cdot}CO_2H$ added. P. W. Clutterbuck.

Production of equimolecular amounts of glycerol and pyruvic acid in the cell-free fermentation of glucose. M. Kobel (Biochem. Z., 1931, **243**, 406—415; cf. A., 1931, 393).—In order to cause the decomp. of glucose by cell-free yeast-maceration juice to assume the fourth form of fermentation it is sufficient to add Na_2HPO_4 until the p_H is 6·9 and, when the juice is very active, to delay the start of the experiment. At first the inorg. phosphate of the juice is almost quantitatively converted into org. P compounds. Then hydrolysis of the esters sets in and accumulation of pyruvic acid takes place. Even when the experiment is prolonged about half of the combined PO_4''' remains as such. Glycerol and pyruvic acid are produced in equimol. amounts and at the same time normal conversion of the sugar into CO_2 and EtOH occurs. W. McCartney.

Decarboxylation of α-keto-*n*-valeric acid. E. Hofmann (Biochem. Z., 1931, **243**, 429—434).—α-Keto-*n*-valeric acid is rapidly (3 hr.) decarboxylated to the extent of 80% by yeast under the same conditions as is pyruvic acid and the amount of butaldehyde which can be recovered after 7 hr. is 73% of the calc. quantity. Thereafter the amount decreases, but there is no production of butyroin. The sulphite compound of the acid is decarboxylated in the same way to the extent of 75% (cf. Dirscherl, A., 1931, 1457). W. McCartney.

Yeast fat. I. G. Weiss (Biochem. Z., 1931, **243**, 269—273).—Yeast fat contains *d*-valeric acid (probably a mixture of optically active and inactive acids), a fatty *acid*, m. p. 88·5°, mol. wt. 379 (probably a C_{24} acid), and (probably) an unsaturated oxidised acid of mol. wt. about 346. Unsaturated OH-acids of high mol. wt. are also present. W. McCartney.

Chemistry of the white rots of wood. II. Effect on wood substance of *Armillaria mellea* (Vahl), Fr., *Polyporus hispidus* (Bull.), Fr., and *Stereum hirsutum*, Fr. W. G. Campbell (Biochem. J., 1931, **25**, 2023—2027).—Analytical data of original and of decayed wood are given. In every case there is no marked increase in the total alkali-solubility of the major components of wood substance. In the case of *A. mellea* it is due to the fact that the pentosans not in the cellulose become less sol. in 1% NaOH as decay proceeds. S. S. Zilva.

Biological decomposition of plant materials. III. Physiological studies of some cellulose-decomposing fungi. A. G. Norman (Ann. Appl. Biol., 1930, **17**, 575—613; cf. A., 1930, 261; this vol., 93).—The optimum temp. of development of cellulose-destroying fungi is higher than that usual for fungal growth. The availability of various N and C compounds to the various species is recorded. Pentoses, although readily utilised, are less suitable sources of C than hexoses. CO_2 formation and heat evolution during fermentation are closely parallel. The period of max. heat production corresponds with that of rapid destruction of hemicellulose.

A. G. Pollard.

Soluble enzymes secreted by *Hymenomycetes*. Alcoholic constituents of essential oils and anti-oxygenic function. L. Lutz (Compt. rend., 1931, **193**, 1220—1221).—The changes produced in a medium containing the alcoholic constituent and methylene-blue on the growth of *Coriolus versicolor*, *Stereum hirsutum*, and *S. purpureum* are recorded.

C. C. N. Vass.

Biochemistry of micro-organisms. J. J. van de Velde and A. Verbelen (Bull. Acad. roy. Belg., 1931, [v], **17**, 1262—1273).—The p_H vals. (given in parentheses, the first being that of the original medium) resulting when *Penicillium glaucum*, *Phycomyces nitens*, *Aspergillus niger*, and *Oidium lactis* are grown on carrot (5·30, 7·27, 5·93, 5·80, 7·80), potato (6·46, 7·43, 6·08, 4·48, 7·23), pork (6·58, 8·62, 8·85, 6·68, 7·78), and fish (6·86, 8·42, 7·74, 6·52, 8·44) for 2 months at 25°, have been determined. The proteins, fats, and ash in the dried H_2O-insol. products and the sugars and ash in the dried H_2O-sol. products have been determined in each case. The results indicate that the quant. metabolism of micro-organisms is influenced more by the properties of the medium than by any specificity. J. W. Baker.

Production of oxalic acid from uronic acids by *Aspergillus niger*. E. Hofmann (Biochem. Z., 1931, **243**, 423—428).—The K salts of *d*-glycuronic, α-*d*-galacturonic, and tetragalacturonic acids are completely decomposed in 5 weeks by *A. niger*. The only org. acid produced is $H_2C_2O_4$, of which large amounts (up to 20% of the theoretical in the case of galacturonic acid) are obtained. W. McCartney.

Adsorption of potassium by *Penicillium glaucum* in Raulin's solution with increasing quantities of potassium nitrate. Bretin, P. Manceau, and Rey (Compt. rend. Soc. Biol., 1931, **106**, 197—198; Chem. Zentr., 1931, ii, 257).

Metabolism of sugar, phytosterol, and lecithin in *Penicillium glaucum* grown in Raulin's solution with increasing quantities of potassium nitrate. Bretin, P. Manceau, and Cochet (Compt. rend. Soc. Biol., 1931, **106**, 195—196; Chem. Zentr., 1931, ii, 257).—In a medium containing sucrose, tartaric acid, NH_4NO_3, $(NH_4)_2SO_4$, $(NH_4)_3PO_4$, K_2CO_3, $MgCO_3$, $MnCO_3$, and $ZnSO_4$, the sugar assimilation and the production of lecithin are retarded, whilst the formation of phytosterol is accelerated, by addition of KNO_3. When larger quantities of KNO_3 are added the formation of both phytosterol and lecithin is retarded. A. A. Eldridge.

Biochemistry of micro-organisms. XXII. Isolation and characterisation of ergosterol from *Penicillium puberulum*, Bainier, grown on synthetic medium with dextrose as sole source of carbon. J. H. Birkinshaw, R. K. Callow, and C. F. Fischmann (Biochem. J., 1931, **25**, 1977—1980).—Ergosterol was isolated. S. S. Zilva.

Action of certain moulds on solutions of aldoses. II. A. Angeletti and C. F. Cerutti.—See this vol., 145.

Specificity in fermentation. M. Schoen (Ann. Inst. Pasteur, 1931, **47**, 690—742).—A general discussion of the chemical reactions which take place in the degradation of glucose by micro-organisms.

W. O. Kermack.

Decomposition of sugars by Lindner's *Termobacterium mobile*. C. Neuberg and M. Kobel (Biochem. Z., 1931, **243**, 451—460; cf. Lindner, B., 1931, 776).—The bacterium decarboxylates pyruvic acid, at least 60% of it being converted into MeCHO and CO_2. From glucose by the action of the bacterium 24·4% of the theoretical amount of MeCHO is obtained. In the presence of phosphate the dried micro-organism causes phosphorylation of glucose. Mg hexosediphosphate is decomposed with elimination of H_3PO_4, and fermentation and Ba hexosemonophosphate are dephosphorylated by the bacterium, but glucose is not fermented unless cozymase from yeast is first added. W. McCartney.

Mechanism of the primary attack on hexoses by lactic acid bacteria. I. C. Fromageot and J. Roux (Biochem. Z., 1931, **243**, 175—190).—The early stages of the fermentation of sugars by *B. bulgaricus* are followed in terms of the manometrically determined CO_2 liberated by reaction of the formed lactic acid with $NaHCO_3$. Curves show the rate of fermentation of glucose, mannose, fructose, galactose, and lactose. For all these sugars, the curves show an induction period followed by a period of vigorous fermentation and finally by a period in which the reaction almost ceases. The ordinates for this third stage are different for the different sugars, but always below the theoretical. The fermentation velocities are in the following order: fructose>mannose>glucose>galactose. Lactose shows a greater induction period, the curve then rising more quickly than with galactose. Fructose has the shortest induction period. In comparing the kinetics of the lactic acid fermentation of glucose and mannose, the same bacterial wt. under the same conditions did not give analogous results. The longer the culture was kept on milk or bouillon, the more did the fermenting power decrease. The smaller was the fermenting power, the less was the power to multiply in bouillon, whereas the power to grow in milk remained normal. The decrease of activity is accompanied with an increase of induction period. Phosphate causes an activation and a decrease of induction period only with bacteria showing decreased activity.

P. W. Clutterbuck.

Bacterial decomposition of glucose ureide. E. Hofmann (Biochem. Z., 1931, **243**, 416—422).—Although many bacteria have no effect on the ureide, manure from hen-runs contains one or two organisms which completely decompose the substance and its constituents. These organisms have not yet been fully characterised. When the decomp. is complete almost all the N of the ureide, about half of it as NH_3, is found in the culture fluid.

W. McCartney.

Dismutation of aldehyde and acetic fermentation. E. Simon (Biochem. Z., 1931, **243**, 401—405; cf. Bertho and Basu, A., 1931, 394).—Confirmation of the view that the dismutation can proceed aërobically has been obtained by the author and by Tanaka (this vol., 94). W. McCartney.

Relation of urea fermentation to oxidation–reduction potential of the medium. S. I. Kuznetzov (Trans. Sci. Inst. Fertilisers, Moscow, 1930, No. 76, 128—131).—The fermentation of urea may take place at r_H 28—0·8, *i.e.*, under aërobic and anaërobic conditions. When N_2 is used instead of H_2 the methods accepted for determining anaërobic conditions gave entirely different results.

Chemical Abstracts.

Liberation of elementary nitrogen by bacteria. N. W. Barritt (Biochem. J., 1931, 25, 1965—1972).—It is confirmed that N_2 is liberated by soil bacteria during denitrification and that there is no evolution of N_2 from org. compounds under anaërobic conditions in absence of oxidised N nor from oxidised N in absence of oxidisable org. compounds. The reduction of NO_3' to NO_2' is effected most rapidly in presence of compounds of low C/N ratio and the formation of N_2 is strictly confined to the reduction of oxidised N provided the reaction of the medium does not fall below p_H 6·5. The production of N_2 from org. compounds does not occur by bacterial action, but only indirectly by the interaction between free HNO_2 and NH_2-compounds, both of which may be produced simultaneously by bacteria. Free HNO_2 is liberated from nitrites by org. acids and H_2CO_3, but does not effect the decomp. of NH_2-acids unless the p_H of the medium is less than 6·0. The presence in a culture of readily available carbohydrates may result in a loss of N_2 from org. matter by the indirect process mentioned above. In Kjeldahl determinations of solutions of org. N the presence of NO_2' results in a loss of NH_2-N during the acid digestion. Threre is no liberation of N_2 by the decomp. of NH_4NO_2 in culture solution at room temp.

S. S. Zilva.

Effect of certain soil bacteria on the growth of root nodule bacteria. K. Konishi (Mem. Coll. Agric. Kyoto, 1931, No. 16, 17 pp.).—In soil cultures the development of the root-nodule bacteria associated with lucerne is not inhibited by *B. subtilis*, *B. mycoides*, *B. prodigiosus*, *B. fluorescens*, *B. coli*, *B. megatherium*, and *B. aërogenes*. In liquid cultures *B. coli* and *B. subtilis* exert an inhibitory influence, the last-named not only towards the lucerne bacteria, but also towards those associated with pea and soya bean. The inhibitory influence was less in liquid cultures containing $CaCO_3$. W. G. Eggleton.

Biological degradation of arginine to citrulline. D. Ackermann (Z. physiol. Chem., 1931, **203**, 66—69).—Citrulline, m. p. 220—222° (cf. A., 1930, 1224), is formed by the action of putrefactive bacteria on arginine. J. H. Birkinshaw.

Phosphorus distribution in bacterial cultures. II. J. Gordon and K. E. Cooper (Brit. J. Exp. Path., 1931, **12**, 234—238).—The org. P present in *B. coli* grown in media free from org. P consists of approx. 86% of org. P other than lipin and 14% of lipin-P. The bacteria appear to be capable of synthesising lipin-P from inorg. sources.

Chemical Abstracts.

Multiplication of micro-organisms. Modification brought about in the composition of various liquid media by the growth of micro-organisms (*B. pyocyaneus*). J. Régnier and R. David (Compt. rend., 1931, **193**, 1487—1490).—*B. pyocyaneus*, grown in various media, causes a rise in surface tension, an increase in alkalinity due to formation of NH_3, and a decrease in C, total N, NH_2-N, and total P. The cessation of growth which occurs about the 11th day does not depend on the exhaustion of any of the nutritive factors so far investigated.

W. O. Kermack.

Distribution of electrolytes in serum during immunisation. K. C. Berthelsen and P. P. Murdick (J. Immunol., 1931, **21**, 69—84).—The diffusible Ca in the serum of horses undergoing immunisation with diphtheria toxin decreased after injection of large amounts. The total Ca and total base behaved somewhat similarly. Considerable fluctuation in total and diffusible P was observed.

Chemical Abstracts.

Diphtheria toxin produced in synthetic media. M. E. Maver (J. Infect Dis., 1931, 49, 1—8).—Diphtheria bacilli, grown on a modified Braun–Hofmeier synthetic medium, synthesise a protein simultaneously with the production of toxin; in an electric field both migrate to the anode at p_H 4·05 and to the cathode at p_H 3·75, and they are simultaneously destroyed by trypsin and pepsin. The toxin fraction of the filtrate is identical with, or closely associated with, a protein. Chemical Abstracts.

Acid precipitation of diphtheria toxin. W. E. Bunney, J. Cianciarulo, and M. Kiamil (J. Immunol., 1931, 20, 417—431).—The toxin is purified by adding dil. HCl (1 : 10) to max. pptn., centrifuging, washing, and dissolving the ppt.

Chemical Abstracts.

Purification of diphtheria toxin. S. Ohiyama (J. Biochem., Japan, 1931, 13, 255—272).—Toxin conc. by adsorption on $Zn(OH)_2$, $Zn_3(PO_4)_2$, or Ca, Sr, or Ba hydroxides or phosphates gives no reaction for protein or sugar, although trypsin destroys it. Probably the toxin is constitutionally related to protein. Chemical Abstracts.

Speed of flocculation of diphtheria toxin. W. E. Bunney and M. Kiamil (J. Immunol., 1931, 20, 433—445).—A toxin which on acidification yields a slight ppt. (flocculating slowly in the Ramon test), when treated with the toxin of a foreign protein pptg. at the same p_H, yields a rapidly flocculating ppt. Hence the toxin is probably merely adsorbed on pptd. protein. Chemical Abstracts.

Flocculation-reaction time in course of immunisation and quantitative and qualitative changes in the proteins. K. C. Berthelsen (J. Immunol., 1931, 21, 43—67).—The increase in flocculation-reaction time during immunisation of horses for production of diphtheria antitoxin was not related to quant. changes in the protein fractions. Qual. differentiation of the protein complexes could not be demonstrated. Chemical Abstracts.

Relationship of surface phenomena to the reaction of toxin and antitoxin, with toxin produced in an infusion-free peptone medium. K. C. Berthelsen (J. Immunol., 1931, 21, 21—41).—Toxin–antitoxin flocculation first takes place at the liquid–air surface, where the surface energy is minimal. The shorter is the flocculation-reaction time the higher is the surface tension. An antitoxic serum in which the protein particles had been denatured by heat showed parallelism between flocculation-reaction time and surface tension. Chemical Abstracts.

Oxidation–reduction potentials of *Staphylococcus* cultures. II. Effect of bacteriophage. L. F. Hewitt (Biochem. J., 1931, 25, 2068—2071).—The potential of these cultures falls initially even in the presence of bacteriophage despite the delay in the proliferation of the bacteria. When bacteriophage is present the potential soon ceases to fall and commences to rise, but a further fall in potential occurs at the time when growth first becomes apparent in the cultures. S. S. Zilva.

Protein fractions of a scarlatinal strain of *Streptococcus hæmolyticus*. M. Heidelberger and F. E. Kendall (J. Exp. Med., 1931, 54, 515—531).—The extraction of a labile nucleoprotein is described. The product differs from the fractions prepared by subsequent alkaline extraction of the cell residues and from " nucleoprotein " obtained in the usual way. It is sensitive to weak alkalis, readily losing nucleic acid. The protein degradation products resemble the alkali-extracted protein fractions of the cell residues. Chemical Abstracts.

Formation of bacterial proteases, especially in synthetic media. R. B. Haines (Biochem. J., 1931, 25, 1851—1859).—Sterile filtrates of broth cultures of *B. mesentericus* and a *Pseudomonas* attack commercial caseinogen or gelatin readily, but have little action on native ovalbumin. Mixtures of salts of Ca and Mg or Mg salts alone, but not Ca salts alone, stimulate the growth of micro-organisms in simple synthetic media. Proteases are formed in simple synthetic media with NH_4Cl as the source of N if Ca and Mg salts are present. Little or no protease formation occurs in presence of Mg salts alone despite good growth. Protease formation is stimulated by these salts in a medium containing NH_4 lactate and asparagine. The influence of Ca and Mg salts on protease formation cannot be explained on the basis of stimulation of growth only.

S. S. Zilva.

Chemo-immunological studies on conjugated carbohydrate proteins. IV. Synthesis of the *p*-aminobenzyl ether of the soluble specific substance of type III pneumococcus and its coupling with protein. W. F. Goebel and O. T. Avery. **V. Immunological specificity of an antigen prepared by combining the capsular polysaccharide of type III pneumococcus with foreign protein.** O. T. Avery and W. F. Goebel (J. Exp. Med., 1931, 54, 431—436, 437—447).—IV. The p-*nitrobenzyl ether* (2·99% N) has [α] —26·5°, acid equiv. 480. Reduction with $Na_2S_2O_4$ in nearly neutral solution gives the p-*aminobenzyl ether*, [α] —28·5°, acid equiv. 453.

V. Type sp. antipneumococcus immunity has been induced in rabbits with the antigen.

Chemical Abstracts.

Lipins of tubercle bacilli. XXIV. Acetone-soluble fat of bovine tubercle bacillus. M. L. Burt and R. J. Anderson. **XXV. Phosphatide fraction of timothy bacillus.** M. C. Pangborn and R. J. Anderson (J. Biol. Chem., 1931, 94, 451—463, 465—472).—XXIV. The fat consists mainly of free fatty acids. After hydrolysis by alcoholic KOH and removal of fatty acids, the aq. solution contains an unidentified polyhydric alcohol and a trace of volatile (butyric) acid. The unsaponifiable matter (10%) is unsaturated, but gives no definite sterol reactions. The fatty acids have been separated into (*a*) a solid fraction consisting of palmitic, cerotic, and hexacosoic acids, fractionated as Me esters, (*b*) a liquid unsaturated fraction, probably a mixture of linoleic and linolenic acids, and (*c*) a liquid saturated fraction containing tuberculostearic acid and an optically inactive acid of higher mol. wt. than stearic acid.

XXV. Timothy phosphatide yields, on acid hydrolysis, 60% of Et_2O-sol. and 40% of H_2O-sol. material. The former fraction comprises palmitic acid (20% of whole phosphatide), a liquid saturated optically inactive acid (18%), and unsaturated acids (5·6%), which yield a mixture of stearic and palmitic acids on reduction. The H_2O-sol. fraction contains glycerophosphoric acid (10%), mannose (9%), inositol (2%), and a residue of unidentified reducing sugar and glycerol. A. Cohen.

Composition of the active principle of tuberculin. XIII. Anaphylactogenic action of the

protein from filtrates of acid-fast bacteria. J. H. Lewis and F. B. Seibert (J. Immunol., 1931, 20, 201—220).—The proteins isolated from filtrates of acid-fast bacterial cultures on a synthetic medium are actively anaphylactogenic. A definite antigenic relationship exists between human, bovine, and avian tubercle bacillus proteins, but none exists between those of tubercle bacillus and timothy bacillus. Chemical Abstracts.

Stability of solutions of tuberculin. E. Fernbach (Compt. rend., 1931, 193, 1486—1487).—A dil. solution of tuberculin in saline containing PhOH retained its activity without significant loss for 25 years, having been preserved in sealed tubes at 20°. W. O. Kermack.

Specific cytotoxic action of tuberculin in tissue culture. J. D. Aronson (J. Exp. Med., 1931, 54, 387—397). Chemical Abstracts.

Anaphylactic and tuberculin types of hypersensitiveness. II. Influence of the nature of the antigen on the development of different types of hypersensitiveness. L. Dienes (J. Immunol., 1931, 20, 333—345).—Differences between cryst. ovalbumin and ovoglobulin are described. Chemical Abstracts.

Differential stain for acid-fast bacteria and spores. V. Burke, R. Dickson, and S. Philips (Stain Tech., 1932, 7, 21—24).—After staining with carbol–fuchsin the slide is immediately covered with a saturated solution of malachite-green in $COMe_2$ for 3—5 min. It is then washed and examined. If the smear is too dense it is dried for 3 min. and decolorised in NH_3 vapour. On exposure to air the green colour returns; this can be prevented by making the smear alkaline with Na_2CO_3. In order to detect tubercle bacilli in thick sputum smears the slide is stained with carbol–fuchsin, decolorised with 30% aq. phenoldisulphonic acid, washed, and examined at once. The organisms appear red on a colourless background. H. W. Dudley.

Bacterial fluorescence in various media. I. Inorganic substances necessary for bacterial fluorescence. F. R. Georgia and C. F. Poe (J. Bact., 1931, 22, 349—361).—Mg, phosphates, and sulphates are essential for pigment production by bacteria. Sufficient Mg may be dissolved from soft glass tubes and may occur even in highly purified reagents. The production of fluorescence may be utilised as a very delicate test for $Mg^{\cdot\cdot}$, PO_4''', and SO_4''. A. G. Pollard.

"Resting" bacteria. B. R. Sandiford and W. R. Wooldridge (Biochem. J., 1931, 25, 2172—2180).—Thick suspensions of bacterial cells which have previously been well shaken in physiological saline or Ringer's solution ("resting bacteria") consist in part of cells which will proliferate when inoculated on suitable media. The total no. of cells remains practically const. throughout long periods of anaërobic incubation at 45° in presence of various substrates with or without methylene-blue. In absence of the dye the no. of viable organisms steadily decreases, whereas in presence of methylene-blue the viable count first shows a fall, followed by a temporary rise, subsequently falling more slowly. The enzymic activity of these preps. towards the various substrates remains practically const. throughout incubation. Both viable and dead cells are enzymically active. The no. of living cells may sometimes increase under conditions thought to inhibit growth. S. S. Zilva.

Effect of sodium ricinoleate on the *Gonococcus*. C. P. Miller, jun., and R. Castle (J. Bact., 1931, 22, 339—348).—Na ricinoleate solutions (1 : 20,000) inhibited the growth of *Gonococcus*, which was almost completely dissolved by 0·1 and 1·0% solutions of the soap. Na ricinoleate increases the lethal action of the organism to mice. A. G. Pollard.

Biochemical action of arsenic. J. Paskuj (Magyar Chem. Fol., 1930, 36, 111—118; Chem. Zentr., 1931, ii, 73).—As was adsorbed only from H_3AsO_4 and salvarsan by the spores used; the As did not kill the spores, but hindered their germination. A. A. Eldridge.

Behaviour of Gram-negative and -positive bacteria towards distilled water and the action of very small quantities of salts of heavy metals. K. Tauchert (Z. Desinfekt., 1931, 23, 213—232; Chem. Zentr., 1931, ii, 257—258).—In oligodynamic experiments the dilution water must be completely free from nutrients and metallic impurities. The highly toxic action of salts of heavy metals is regarded as an oligodynamic action. Only with salts of tervalent metals was there a difference between Gram-positive and -negative bacteria, the former being somewhat more resistant. A. A. Eldridge.

Bactericidal water by filtration and sterilisation. G. Lakhovsky (Compt. rend., 1932, 194, 137—139).—H_2O unfit for drinking, passed through a candle which had been previously treated with AgCl at 1200° for 24 hr., is rendered non-toxic and sterile and possesses bactericidal activity. Analysis of the H_2O shows no Ag, and its bactericidal action is believed to be due to ionisation produced by contact of the dissolved matter with the Ag during filtration, since after filtration the p_H increases. On boiling, the bactericidal action is lost. A. Lawson.

Blood corpuscles and absorption of certain nutrients and hormones, especially adrenaline. M. Gedroyc and W. Koskowski (Compt. rend. Soc. Biol., 1930, 105, 409—412; Chem. Zentr., 1931, i, 2492).—When solutions of adrenaline or histamine are allowed to act on blood-corpuscles for approx. 30 min. a part of the hormone is absorbed, and after the corpuscles are washed the biological action of the hormone can readily be detected. This absorption must be important in transporting hormones and partly explains the rapid disappearance from the plasma of adrenaline injected into the blood-vessels. L. S. Theobald.

[Pharmacology of] sparteine and adrenaline. R. Hazard (Compt. rend., 1932, 194, 130—132).—Sparteine increases and prolongs the hypertensive action of adrenaline by its action on the vagus nerve-endings and by potentiating the action of adrenaline on the cardiac and vascular sympathic nerve-endings. A. Lawson.

Determination of hexosemonophosphate in muscle. G. T. Cori and C. F. Cori (J. Biol. Chem., 1931, **94**, 561—579).—Rat muscle is treated with aq. $CCl_3\cdot CO_2H$ and the reaction of the extract adjusted to p_H 8·2 by $Ba(OH)_2$, whereby PO_4''', adenosinetriphosphate, and the fraction containing undetermined P are pptd. Decomp. of the ppt. by H_2SO_4 and repptn. at p_H 8·2 removes some hexosephosphate included in the Ba ppt. The combined liquids are then pptd. by 80% EtOH in presence of aq. NH_3 and the reducing power and P content of this ppt. determined. Incubation of the muscle in $NaHCO_3$ solution at 37° results in formation of PO_4''' from 92·4% of the adenosinetriphosphate and undetermined P fraction, whilst only 15—30% of the hexosephosphate is converted, accounting for 7% of the inorg. P liberated. Thus, whilst decomp. of added Embden's ester is quant., the liberated inorg. P other than that due to "pyrophosphate" is not formed by total decomp. of hexosephosphate present in the muscle, but mainly from adenylic acid derived from adenosinetriphosphate (cf. A., 1929, 347). F. O. Howitt.

Influence of adrenaline and insulin injections on hexosephosphate content of muscle. C. F. Cori and G. T. Cori (J. Biol. Chem., 1931, **94**, 581—591).—The average hexosephosphate content of muscle removed from rats under amytal anæsthesia is 0·0533% (as hexose). This val. rises as high as 0·20% immediately after death by stunning, bleeding, etc. Subcutaneous administration of adrenaline is followed 15 min. later by a rise in the hexosephosphate level, attaining a max. of 0·109% after 1 hr. and returning to normal within 4 hr. A similar phenomenon occurs with insulin injection, but is inhibited by simultaneous glucose administration or by adrenalectomy. Hence the secondary liberation of adrenaline is responsible for the increase attending insulin hypoglycæmia. In no instance is there an accumulation of hexosediphosphate or fission of P from adenosinetriphosphate. Glucose-feeding does not change the hexosephosphate content of muscle, hence the decrease in urinary P following ingestion of glucose is not explained on these grounds as it is when adrenaline or insulin is injected. The intermediary metabolism of the glycogen–lactic acid transformation is discussed. F. O. Howitt.

Metabolism of animals on carbohydrate-free diet. III. Effect of alkali on the sensitivity towards insulin of albino rats. A. Hynd and D. L. Rotter (Biochem. J., 1931, **25**, 1893—1901; cf. A., 1931, 771).—Rats previously rendered resistant to insulin by a cheese diet soon become responsive after the addition of $NaHCO_3$, but not of an equiv. of $KHCO_3$. $NaHCO_3$ is also more efficient in this respect when a carbohydrate-free diet is used. The difference in behaviour of the two salts bears no relationship to the carbohydrate stores of the animal. Administration of $NaHCO_3$ does not reduce the liver- or muscle-glycogen of carbohydrate-fed rats, and it favours rather than inhibits the action of insulin. An NH_4Cl acidosis is accompanied by marked resistance to insulin, which readily disappears after the addition of either $NaHCO_3$ or $KHCO_3$ to the diet.
S. S. Zilva.

Fate of the thyroid hormone in hyperthyroidised animals. II. Excretion of thyroid hormone by the dog after oral administration of dried thyroid. III. Excretion of thyroid hormone after oral administration of thyroxine. G. Asimov and E. Estrin. **IV. Hyperthyroidisation of fowls with a single dose of thyroid and determination of iodine in tissues.** G. Asimov, E. Estrin, and S. Miletzkaja (Z. ges. exp. Med., 1931, **76**, 380—398, 399—408, 409—418; Chem. Zentr., 1931, ii, 75).—II. Most of the I is excreted in 24 hr.; I appears in the urine and bile after 30 min. and is max. after 12—16 and 15—17 hr., respectively, the ratio of amounts excreted being 20 : 1. Part is unabsorbed. The urinary I is biologically inactive, but the bile-I accelerates the metamorphosis of axolotls.

III. Most of the I is excreted in 24 hr. The greater part is unabsorbed, and approx. equal quantities are excreted in the urine and bile. The max. is reached in about 5 hr. The urinary I is biologically inactive, and the bile-I is biologically active.

IV. 1·29% of the I administered is found in the egg-yolk; it has practically no biological activity. I is also found in the thyroid, kidneys, liver (as thyroxine), blood, and pancreas. Little I is present in the muscle, fat, brain, and sexual organs.
A. A. Eldridge.

Effect of administration of sugar and insulin on the liver-glycogen of animals receiving thyroxine. G. Knittel (Z. ges. exp. Med., 1931, **76**, 362—368; Chem. Zentr., 1931, ii, 75—76).—The fall in liver-glycogen, observed in guinea-pigs on administration of thyroxine, is arrested by injection of fructose and insulin, but the effect on body-wt. is unchanged. A. A. Eldridge.

Anterior pituitary gland and iodine content of the thyroid gland. A. Loeser (Arch. exp. Path. Pharm., 1931, **163**, 530—533).—Injection of suspensions of powdered, $COMe_2$-dried, anterior pituitary gland into dogs results in a decrease of I content of the thyroid gland in addition to morphological changes. F. O. Howitt.

Effect of the ovarian (follicular) hormone on the sensitivity of the uterus towards the posterior pituitary hormone. F. Siegert (Klin. Woch., 1931, **10**, 734—737; Chem. Zentr., 1931, ii, 258—259).—The hormones are antagonistic.
A. A. Eldridge.

Œstrus-producing hormones. G. F. Marrian and A. Butenandt (Science, 1931, **74**, 547).—A discussion. L. S. Theobald.

Occurrence of ovarian hormone in urine. E. Glimm and F. Wadehn (Biochem. Z., 1931, **243**, 97—99).—The authors' previously published results on the hormone contents of the urines of children, men, and women have often been higher than those of other authors. The discrepancy is due to differences in the methods of isolation and biological assay.
P. W. Clutterbuck.

Female sexual hormone in unicellular animals. E. E. Bauer (Arch. exp. Path. Pharm., 1931, **163**, 602—610).—Injection of EtOH extracts of the protozoon *Colpoda Steini* induces œstrus in spayed mice

within 40 hr. Vegetable matter used for the culture of the protozoa is inactive. Such extracts also cause paralysis in mice, affect the frog's heart in a manner similar to that of bile acids, and exhibit a weak hæmolysing action on washed ox erythrocytes.
F. O. Howitt.

Comparison of the rat and mouse units in the assay of the female sex hormone. T. J. Becker, C. H. Mellish, F. E. D'Amour, and R. G. Gustavson (J. Pharm. Exp. Ther., 1931, 43, 693—695).—The rat and mouse units of œstrin are approx. equal.
W. O. Kermack.

Vitamin-*A* from fish oils. II. P. Karrer, R. Morf, and K. Schöpp (Helv. Chim. Acta, 1931, **14**, 1431—1436).—The unsaponifiable matter of the oil from *Scombresox saurus* is purified as described previously (A., 1931, 1463). The resulting viscous oil (vitamin-*A*) has *M* 300—320, the composition $C_{20}H_{30}O$ or $C_{22}H_{32}O$, gives a p-*nitrobenzoate* and an *acetate* (hydrolysed by EtOH–KOH at 60° to the original material), is oxidised by O_3 giving a considerable amount of geronic acid, and by $KMnO_4$ and CrO_3, yielding AcOH ≡ 9·7 and 16·3% of C·CMe groups, respectively. Catalytic reduction affords a *product*, $C_{20(or\ 22)}H_{40}O$, which can be distilled in vac. Formulæ are suggested.
H. Burton.

Vitamin-*A* and carotene. VIII. High-potency vitamin-*A* concentrates. T. Moore (Biochem. J., 1931, 25, 2131—2135).—Although the initial blue vals. of liver oils of rats which previously received large amounts of carotene in the form of red-palm oil and of turbot and sole oils varied widely, little difference could be detected in the activities of the final concentrates from these sources, which approached an average val. of 2400 B.U. per mg. (pharmacopœia colour val. 45,000) in the $SbCl_3$ test corresponding with a min. dose of about 0·001 mg. in rat-growth experiments.
S. S. Zilva.

Effect of mineral oil administration on the nutritional economy of fat-soluble vitamins. I. Vitamin-*A* of butter-fat. R. W. Jackson (J. Nutrition, 1931, 4, 171—184).—With rats, mineral oil causes considerable loss of vitamin-*A* to the animal organism if the oil is mixed with butter-fat prior to digestion. If the oil is administered separately there is only a very slight diversion of vitamin-*A*.
Chemical Abstracts.

Effect of xanthophyll on the growth of rats. H. von Euler, P. Karrer, and M. Rydbom (Helv. Chim. Acta, 1931, **14**, 1428—1431).—Rats grow during 4 weeks on a diet supplemented by xanthophyll, m. p. 192° (dose 0·037 mg.). After this time growth diminishes and then ceases; a continuation can usually be effected by adding carotene in a quantity which is normally insufficient. Xanthophyll cannot replace carotene.
H. Burton.

Distribution of the vitamin-*B* complex. III. Fruits. M. H. Roscoe (Biochem. J., 1931, 25, 2050—2055).—The vitamin-B_1 content of the orange is the highest, being 1/5 that of yeast (dry wts.). The val. of tomato is rather less than 1/10 that of yeast, the banana 1/20, and apple still lower. The vitamin-B_2 content of orange, tomato, and banana is rather less than 1/10 and of apple 1/20 that of yeast (dry wts.). These vals. are compared with those of other foodstuffs.
S. S. Zilva.

Effect of coprophagy in rats deprived of the vitamin-*B* complex. M. H. Roscoe (Biochem. J., 1931, **25**, 2056—2067).—The life of rats receiving cooked diets deficient in the vitamin-*B* complex or its constituents and containing sol. starch was prolonged considerably when they ate their fæces, whether sterilised or not, and in some cases growth also took place. Death finally occurred as a result of neuritis due to vitamin-B_1 deficiency. A preliminary week of depletion during which coprophagy was not permitted did not prevent this prolongation of life. Growth did not occur when less than 70% of the fæces was consumed and was not proportional to increased consumption. This phenomenon is probably due to the fact that the *B*-vitamins are synthesised by bacteria in the gut. The synthesis is stimulated by the presence in the diet of a heat-stable factor contained in the autoclaved yeast extracts differing from the *B*-vitamins. Refection is a condition distinct from that observed in coprophagous rats fed on cooked diets containing sol. starch.
S. S. Zilva.

Beriberi quotient (*Qb*) in nutrition with polished rice and autoclaved grain. V. Famiani (Atti R. Accad. Lincei, 1931, [vi], 14, 206—209).—With pigeons fed on polished and washed rice, or on rice autoclaved either dry or wet or in presence of alkali, no appreciable differences are observed in the beriberi quotient or in the symptoms.
T. H. Pope.

Possibility of obtaining persistent beriberi phenomena in the pigeon by deprivation of vitamin-*B*. G. Amantea and V. Famiani (Atti R. Accad. Lincei, 1931, [vi], 14, 210—214).—By nutrition with food devoid of vitamin-*B*, pigeons develop beriberi phenomena which persist for a long time, even when the birds are subjected to prolonged, energetic treatment with beer yeast, associated with a mixed ordinary diet.
T. H. Pope.

Function of torulin. An *in vitro* effect of antineuritic vitamin concentrates. N. Gavrilescu and R. A. Peters (Biochem. J., 1931, **25**, 2150—2161).—The O_2 uptake of minced pigeon's brain is increased on an average some 40% by performing the determinations in O_2 instead of air in the case of cerebrum and the mixed optic lobes and parts below from the normal brain. With the avitaminous (B_1) brain less or even no increase takes place with the optic lobes and lower parts. In the presence of O_2 the lowered O_2 uptakes previously observed in the brain in avitaminosis-B_1 are more marked. Partial restoration of O_2 uptake *in vitro* is observed on addition of vitamin-B_1 concentrates to the mixed optic lobes and lower parts of the avitaminous pigeon. This catalytic action of the concentrates is due to vitamin-B_1. The effects are not always obtained with the cerebral tissue.
S. S. Zilva.

Effect of autoclaved cow's milk and of vitamins-*B*, -*C*, and -*D* on the growth of goats. W. Catel and G. Pallaske (Jahrb. Kinderheilk., 1931, **81**, 313—340; Chem. Zentr., 1931, ii, 263—264).—

Autoclaved cow's milk causes small variations in the serum-Ca and -P. Addition of "vigantol" considerably improves growth and assimilation. Addition of vitamin-*B* or lemon-juice affords variable results. The results do not require the assumption that a growth vitamin exists. A. A. Eldridge.

Vitamin-*C*. A. W. Owe (Tidsskr. Kjemi Berg., 1931, **11**, 120—124).—The work of Rygh *et al.* has shown that the narcotine present in unripe fruit must be regarded as the precursor of vitamin-*C*. During the ripening of the fruit the *o*-diphenol derivative is formed, which has a strong antiscorbutic action in a daily dose of about 25×10^{-6} g. It cannot yet be considered definitely proved that the *o*-diphenol derivative is identical with vitamin-*C*. H. F. Harwood.

Preparation of vitamin-*C* concentrates from lemon-juice. J. L. Svirbely and C. G. King (J. Biol. Chem., 1931, **94**, 483—490).—The vitamin-*C* of a concentrate prepared from lemon-juice (A., 1930, 119, 381) is extractable by petrol–$COMe_2$ (1 : 1), petrol–BuOH (2 : 1 and 4 : 1), petrol–PrOH (1 : 1 and 3 : 1), AcOEt, BuOH, and PrOH, but not by Et_2O. By the use of such extractants concentrates of 0·03—0·5 mg. of solids per c.c. of lemon-juice are obtained which are fairly stable and appear to contain only one active principle. Passage of NH_3 through solutions in org. solvents destroys the vitamin, which exhibits distinct acidic and reducing properties. F. O. Howitt.

Preparation and storage of vitamin-*C* concentrates from lemon-juice. F. L. Smith, 2nd, and C. G. King (J. Biol. Chem., 1931, **94**, 491—496).—An aq. concentrate (0·09 mg. per c.c. of lemon-juice) prepared by extraction of solids from a $COMe_2$ solution with BuOH and cooling to deposit inactive material (cf. preceding abstract) possessed a strong reducing power and gave a positive test with orcinol and resorcinol. Active ppts. were separated from the concentrate at p_H 7·3—7·5. Citric and formic acids were not superior to HCl as stabilising agents. Storage on solid CO_2 in an atm. of N_2 or CO_2 resulted in complete retention of activity for 2—3 weeks. F. O. Howitt.

Antirachitic vitamin from irradiated ergosterol. A. Windaus and A. Lüttringhaus (Z. physiol. Chem., 1931, **203**, 70—75).—The properties of vitamins-D_1 and -D_2 are reviewed. D_2 corresponds with calciferol (A., 1931, 1464). The so-called vitamin-D_1 is now found to be an additive compound of D_2 and an isomeric alcohol, and is resolved by way of the dinitrobenzoate. J. H. Birkinshaw.

Chemical reaction of antirachitic vitamin. E. Cruz-Coke (Compt. rend. Soc. Biol., 1930, **105**, 238—239; Chem. Zentr., 1931, i, 2497—2498).—A drop of HCl added to an EtOH solution of pure ergosterol at 70—80° gives a white ppt. After irradiation of the ergosterol the pptn. is retarded, and redissolution occurs giving a green solution. This is not the case, however, with non-irradiated material. Further addition of HCl re-forms the ppt. With irradiated ergosterol the amount of HCl necessary for this reaction is proportional to concn. L. S. Theobald.

"Viosterol" and cod-liver oil. E. O. Prather, M. Nelson, and A. R. Bliss, jun. (J. Amer. Pharm. Assoc., 1931, **20**, 1291—1303).—Irradiated ergosterol did not stimulate the growth and development of the body and vital organs (of rats), or prevent infections of the upper respiratory tract or produce the same degree of calcification and growth of the bones as did cod-liver oil. E. H. Sharples.

Vitamin value of cod-liver meal. A. D. Holmes, M. G. Pigott, and D. F. Menard (J. Nutrition, 1931, **4**, 193—201).—Addition of 2% of the best meals is equiv. (chickens) to 0·5% of cod-liver oil. The poorer meals possess little, if any, vitamin val. Chemical Abstracts.

Heterogeneity of natural products. P. Karrer (Collegium, 1931, 700—710).—Examples are quoted of natural products, *e.g.*, gallotannic acid, hitherto considered to be individual chemical substances, which have been resolved into different components, in some cases themselves not single chemical substances. D. Woodroffe.

Dominant starch character in the first generation of the hybrids of two varieties of pea (*Pisum sativum*, L.). L. Bharinghem, M. Bridel, and (Mlle.) C. Bourdouil (Compt. rend., 1931, **193**, 1135—1137).—A comparison of the soluble carbohydrate and starch contents of two varieties of pea together with their hybrids suggests that ovule transmission determines the dominance of the starch content. C. C. N. Vass.

Quantitative methods for growth-promoting substances. H. G. van der Wey (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 875—892).—A correlation is established between the amount of growth-promoting substance administered and the bending in normal plants or dissected coleoptiles. The response to growth-promoting substances of plants after multiple shoot-decapitation is greater than after single decapitation. A high temp. during germination of *Avena* reduces the production of growth-promoting substance. Old plants have less bending power and a lower content of growth-promoting substance than young plants. Formation of growth-promoting substance in the coleoptiles of *Zea mais* (as shown by the bending reaction in *Avena*) is dependent on the length of the coleoptiles. The diffusion of growth-promoting substance from dissected coleoptiles into agar plates for the purpose of estimation is restricted to a certain max. limit. F. O. Howitt.

Mitogenetic radiation. M. Moissejeva (Biochem. Z., 1931, **243**, 67—87).—Further experiments (A., 1931, 1457) are described bringing the no. above 300. An induction in the original sense of Gurwitsch does not exist. P. W. Clutterbuck.

Effect of various chemical treatments of dormant potato tubers on the peroxidase, catalase, p_H, and reducing properties of the expressed juice. J. D. Guthrie (Contr. Boyce Thompson Inst., 1931, **3**, 499—507).—The action of a number of org. substances in breaking the dormant period of potato tubers was not closely correlated with changes produced in the peroxidase or catalase activity p_H, or reducing power of the juices. A probable relationship is indicated between p_H changes and reducing power. Effective potato dips were either S compounds, or those increasing p_H or reducing power of the juices. The latter effect is associated with an increase in SH compounds in the tuber. A. G. Pollard.

Increase of sugar utilisation in *Spirogyra* by means of commercial fertilisers. E. Williams, L. Kneer, G. C. Wickwire, D. J. Verda, and W. E. Burge (Bot. Gaz., 1931, 92, 321—326).—All fertilisers examined increased the utilisation of sugar from culture solutions by *Spirogyra*, N materials being most active in this respect. Where equal applications of urea, $(NH_4)_2SO_4$, $(NH_4)_2HPO_4$, $NaNO_3$, and $Ca(NO_3)_2$ were made, plant responses were in the order of the N contents of these substances. A. G. Pollard.

Oil development in the seed of a growing plant. J. V. Eyre (Biochem. J., 1931, 25, 1902—1908).—In the oil formation in the seed of *Linum usitatissimum* and *L. cribrosum* the acidic constituents are formed first. Whether glycerol is formed at the same time to combine with the fatty acids at a later stage is not established. There is a remarkably rapid oil formation over a period of some 15 days during which a max. of about 36% of oil, calc. on the dry wt. of the seeds, is reached. The unsaturated character of the oil after formation, as measured by its I absorption, continues to increase. S. S. Zilva.

Soya bean. I. Changes of protein during germination in darkness. W. S. Tao and S. Komatsu. **II. Action of enzymes in seedlings on glycinin.** W. S. Tao (Mem. Coll. Sci. Kyoto, 1931, 14, A, 287—292, 293—296).—I. Germination results in loss of wt. mainly due to decrease in fat and nitrogenous matter, in hydrolytic fission of part of the protein, especially globulin, and in liberation of small amounts of NH_3 and urea.

II. The changes in N distribution are due to the action of proteolytic enzymes on glycinin, the protein of the beans. Seedlings exhibit a urease activity greater than that of the seeds. F. O. Howitt.

Nitrogen metabolism of the lupin seedling. P. McKie (Biochem. J., 1931, 25, 2181—2188).—The total N of the lupin seedling in the seed and in the early stages of growth consists of insol. N, protein, and asparagine. A close relationship exists between the decrease of insol. and protein-N and increase of asparagine. Protein synthesis begins after 16 days' growth and is accompanied by a fall in asparagine content and a rise in proteose content. NH_3, amides, NH_2-acids, and NO_3' are absent from ungerminated seed. They appear immediately growth begins, rise to a low max. in a few days, and then maintain const. lower level. S. S. Zilva.

Iodide fission by *Laminaria digitata*. H. Kylin (Z. physiol. Chem., 1931, 203, 58—65; cf. A., 1931, 132).—The " I liberator " present in *Laminaria* extracts is nitrite formed from nitrate by bacterial action. It is not observed when extracts of fresh material are made sterile by boiling or addition of PhMe. J. H. Birkinshaw.

Hemicelluloses of the wood of English oak. I. Effect of the drying of wood on the yields and composition of hemicellulose-*A*. M. H. O'Dwyer (Biochem. J., 1931, 25, 2017—2022).—With increasingly severe conditions of drying, the hot-H_2O and NaOH extracts of the sapwood or heartwood increase in amount and the yields of hemicellulose-*A* decrease. S. S. Zilva.

Detection of woody plant membranes with phloroglucinol and hydrochloric acid. W. Plahl (Z. Unters. Lebensm., 1931, 62, 603—606).—The defatted specimen is pre-extracted with H_2O to remove sol. matter, and treated with a solution containing equal vols. of 2·5% of phloroglucinol in 96% EtOH and chloral hydrate in H_2O (5 : 2), to which 4% HCl (*d* 1·1246) has been added. The colour is a max. after 15 min., and is permanent for a day. J. Grant.

Pectin of tobacco. C. Neuberg and M. Scheuer (Biochem. Z., 1931, 243, 461—471).—A method by which at least part of the pectin can be isolated as pectic acid from the fresh leaves is described. The acid is similar to that obtained from flax and is readily decomposed by tobacco pectase. W. McCartney.

Non-nitrogenous constituents of tobacco smoke. C. Neuberg and J. Burkard (Biochem. Z., 1931, 243, 472—484; A., 1929, 729).—The smoke contains fatty acids (present as salts in the tobacco) and aldehydes and ketones produced by decomp. Rate and temp. of burning of the tobacco, its H_2O content, and the amount of air available for combustion affect the nature and no. of substances produced. The following acids, aldehydes, and ketones can be identified: formic to hexoic acids, C_7 and C_8 acids, traces of unsaturated and OH-acids; CH_2O to PrCHO; $COEt_2$ (2 : 4-*dinitrophenylhydrazone*, m. p. 149—150°), $COPr_2$ (2 : 4-*dinitrophenylhydrazone*), higher and unsaturated ketones. $COMe_2$ is not found. The butyric acid is probably derived from glutamic acid. Substances which yield BzOH on oxidation with Ag_2O are also found. The mixtures of the higher acids and ketones are optically active. Probably the production of the ketones is catalysed by the mineral matter of the tobacco and by the C produced during burning. W. McCartney.

Lævorotatory carbohydrates of the bulbs of *Lycoris squamigera*, Max. H. Belval (Compt. rend., 1931, 193, 891—893).—Lycoroside (see this vol., 100) is not hydrolysed by invertase. The accompanying fructoside has [α] −19°, and after hydrolysis with HCl [α] −67°; it is slowly hydrolysed by invertase. C. C. N. Vass.

Composition of cherry gum. C. L. Butler and L. H. Cretcher (J. Amer. Chem. Soc., 1931, 53, 4160—4167).—The gum used contained H_2O (10·75%), ash (1·5%), and H_2O-sol. material (14·5%); analysis showed ash (1·3%), galactose (27·7%), arabinose (31·6%), other pentoses (as xylose) (24·5%), and uronic acid (10·1%). Acid hydrolysis gives, initially, pentoses and a complex acid (containing glycuronic acid, mannose, and galactose), which is hydrolysed further to galactose and a complex of glycuronic acid and mannose. The acidic nucleus of the gum contains 2 uronic acid units combined with 1 sugar group instead of the 1 : 1-combination found in the aldobionic acids. The mol. proportions of the various constituents are estimated to be arabinose 8, xylose 6, galactose 6, mannose 3, and glycuronic acid 2, whilst the complex acid formed by hydrolysis of the gum with 18% HCl has galactose 6, mannose 3, and glycuronic acid 2. C. J. West (*b*).

Carbohydrate hydrogen sulphate of *Macrocystis pyrifera*. W. L. Nelson and L. H. Cretcher (J. Biol. Chem., 1931, **94**, 147—154).—Extraction of the air-dried fronds with 2% HCl and pptn. with EtOH gives a product containing methylpentose (as fucose) (31·7%), polymeric uronic acid (2·6%), titratable SO_4 (as HSO_4') (17·6%), and inorg. SO_4 (ash) (43·8%). Hydrolysis with 2·5% H_2SO_4 affords fucose. H. Burton.

Presence of a new sugar in dextrorotatory honeys. E. Parisi (Atti R. Accad. Lincei, 1931, [vi], **14**, 125—130).—Conifer honeys, which are dextrorotatory, contain (1) a substance yielding an aldehyde-acid of the glycuronic acid group on hydrolysis, and (2) a non-fermentable *glucobiose*, m. p. 180—203°, $[\alpha]_D$ +110°, *R* 41·7 [*phenylosazone*, m. p. 198—200°, $[\alpha]_D^{12}$ +27·6°; p-*nitrophenylosazone*, m. p. 135°(? 235°)]. The sugar may exist in the flowers of the tree or it may be produced by enzyme action. T. H. Pope.

Constituents of the cluster base and secondary vegetative growth of bearing spurs of the yellow transparent apple. F. S. Lagassé (Proc. Amer. Soc. Hort. Sci., 1931, **27**, 199—205).—The cluster base contains more H_2O and N (sol., insol., and total), total sugars, free reducing sugars, sucrose, polysaccharides, and total carbohydrates, but less starch, than the secondary growth. Application of $NaNO_3$ increases the N, but decreases the carbohydrate, content. Chemical Abstracts.

Globe artichoke, *Cynara scolymus*, L. G. W. Scott (Proc. Amer. Soc. Hort. Sci., 1931, **27**, 356—359).—The (dry) leaves contain sugars 10·89, sucrose 3·42, inulin 1·05%. The relation is reversed in the roots, where the inulin may reach 40% (dry wt.). The NH_3-N content is 1·51—2·86%; little starch is present. Chemical Abstracts.

Chemical examination of roots of *Rauwolfia serpentina*, Benth. S. Siddiqui and R. H. Siddiqui (J. Indian Chem. Soc., 1931, **8**, 667—680).—Fractionation of the substances extracted from the dry root with 90% EtOH gives a *phytosterol* (termed *serposterol*), $C_{30}H_{48}O_2$, m. p. 159—160°, $[\alpha]_D^{23}$ −68·5° in $CHCl_3$, oleic and saturated fatty acids, a mixture of unsaturated alcohols of the composition $C_{25}H_{44}O_2$, and 5 alkaloids (0·5% of dry root) designated (*a*) *ajmaline*, $C_{20}H_{26}O_2N_2+3H_2O$, m. p. 158—160° after losing H_2O at 110° and softening at 150°, $[\alpha]_D^{23}$ +128° in $CHCl_3$ [*hydrochloride* $+2H_2O$, m. p. 133—134°, m. p. (anhyd.) 253—255°; *chloroplatinate*, m. p. 217—218°; *picrate*, m. p. (anhyd.) 223°], (*b*) *ajmalinine*, $C_{20}H_{23}O_4N+H_2O$, m. p. 180—181° [*hydrochloride*, m. p. 240—245° (decomp.) (shrinks at 213° and swells at 235°); *chloroplatinate*, m. p. 254—258° (decomp.); *picrate*, m. p. 200—205° (softens at 175°)], (*c*) *ajmalicine*, m. p. 250—252° (decomp.) [*hydrochloride*, m. p. 260—263° (decomp.) after shrinking at 250°; *picrate*, m. p. 212—215° (decomp.)], (*d*) *serpentine*, $C_{21}H_{23}O_4N+1{\cdot}5H_2O$, m. p. 153—154° [*hydrochloride*, m. p. 260—261° (decomp.) (shrinks at 240°); *chloroplatinate*, m. p. 217—220° (decomp.); *picrate*, m. p. 261—262° (decomp.)], and (*e*) *serpentinine*, m. p. 263—265° [*hydrochloride*, m. p. 260—262°; *chloroplatinate*, m. p. 260—263° (decomp.); *picrate*, m. p. 225—227°]. Colour reactions of the alkaloids are given. H. Burton.

Red colour of the blood-orange. M. B. Matlack (Plant Physiol., 1931, **6**, 729—730).—The presence of acicular crystals of anthocyanin in the juice sacs of blood-oranges is recorded. A. G. Pollard.

Dye of red cabbage. I. H. Willstaedt (Biochem. Z., 1931, **242**, 303—305).—A procedure for the isolation of the dye is described. It is probably an anthocyanin and is pptd. by $Pb(OAc)_2$, but not by $FeCl_3$ or picrolonic acid. It contains about 63% C and 7·0% H. W. McCartney.

Lycopin. L. Cholnoky (Magyar Gyóg. Társ. Ert., 1931, **7**, 95—107; Chem. Zentr., 1931, i, 3015).—Lycopin preps. from *Tamus communis*, *Solanum dulcimara*, and *Lycopersicum esculentum* are identical. No similar associated compounds could be found. A. A. Eldridge.

Anthocyanin of *Oxycoccus macrocarpus*, Pers. K. E. Grove and R. Robinson (Biochem. J., 1931, **25**, 1706—1711).—The anthocyanin was isolated as the chloride $C_{22}H_{23}O_{11}Cl,H_2O$ and identified as a 3-glucoside of peonidin. S. S. Zilva.

Carotene in palm oil. K. Kobayashi, K. Yamamoto, and J. Abe (J. Soc. Chem. Ind., Japan, 1931, **34**, 434—436B).—The colour reactions of C_6H_6 or CS_2 solutions of palm oil with dehydrating agents, such as H_2SO_4, correspond with those of pure carotene. Spectroscopic examination confirms the conclusion that the (principal) pigment of the palm oil is carotene. E. Lewkowitsch.

Microchemical detection of volatile fatty acids in plants. I. G. Klein and H. Wenzl [with N. Kemperling] (Mikrochem., 1931, **10**, 70—89).—Investigation of the anilides of the fatty acids up to C_7 shows these compounds to be unsuitable as a means of identification of the acids in mixtures, but they may be employed to identify certain of the lower acids on a semi-microchemical scale, either by the crystal form or the m. p., when present alone. Similar conditions obtain for the *p*-toluidides. On the semi-micro-scale (50 mg.) the m. p. of the benzylidene derivatives or the monohydrazides may be employed to identify the acids from C_3 to C_5, and the m. p. of the monohydrazides those from C_5 to C_8. H. F. Gillbe.

Wax constituents of the apple cuticle. A. C. Chibnall, S. H. Piper, A. Pollard, J. A. B. Smith, and E. F. Williams (Biochem. J., 1931, **25**, 2095—2110).—The unsaponifiable fraction from the crude plant-wax was treated with phthalic anhydride. The Na phthalates of the primary alcohols were pptd. from the Et_2O solution. After removal of Et_2O the residue was taken up in boiling EtOH, from which the paraffins and ketones crystallised quantitatively, leaving in the mother-liquor the Na salts of the secondary alcohol esters. The mixture of the former can be separated by Channon and Chibnall's method (A., 1929, 729). The following constituents have been identified : *n*-nonacosane, *n*-heptacosane, *d*-κ-nonacosanol, *n*-hexacosanol, *n*-octacosanol, and *n*-triacontanol. S. S. Zilva.

Wax constituents of forage grasses. I. Cocksfoot and perennial rye grass. A. Pollard, A. C. Chibnall, and S. H. Piper (Biochem. J., 1931, 25, 2111—2122).—In the case of cocksfoot the chief constituent is a long-chain primary alcohol (nearly pure *n*-hexacosanol). It contains less than 1% of *n*-tetracosanol and about an equal amount of an unidentified longer-chain alcohol. The same alcohol is present in rye grass wax, but the amount of impurities is greater. Hippocoprosterol is identical with ceryl alcohol. S. S. Zilva.

Seed of *Euphorbia marginata*, Pursh. L. E. Harris and M. C. Gallagher (J. Amer. Pharm. Assoc., 1931, 20, 1281—1286).—The seeds (6·2% H_2O, 4·0% ash) of *E. marginata* gave about 30% of a drying oil having *d* 0·9222, acid val. 7·76, sap. val. 186, I val. 135·66 ; the isolated fatty acids contained linolenic, linoleic, stearic, palmitic, and oleic (trace) acids. E. H. Sharples.

Existence and distribution of caffeine and theobromine in the tissues of guarana. G. Bertrand and P. de B. Carneiro (Compt. rend., 1932, 194, 26—28).—The caffeine content of the kernels and teguments of the dried seeds of *Paullinia cupana* is 4·4 and 2·2%, respectively. Theobromine is not present. The dried leaves, roots (excluding the bark), root bark, stems (excluding the bark), stem bark, flowers, and flower stalks contain 0·38, 0·27, 1·74, 0·19, 0·17, 0, 0%, respectively, of caffeine, and 1·2, 0, 0, 0, 0·98, 1·54, 0·38%, respectively, of theobromine. A. Lawson.

Supposed glutathione of peas. A. Kozlowski (Biochem. Z., 1931, 241, 407—408)..—In the method previously described (A., 1927, 80) a better yield of the substance containing cysteine is obtained by extracting with $COMe_2$ and pptg. with Cu_2O. It is not certain that the substance is identical with the glutathione of yeast. W. McCartney.

Dicarboxylic acid nitrogen of proteins. Alcohol-soluble protein from Ragi (*Eleusine coracana*). M. Damodaran (Biochem. J., 1931, 25, 2123—2130).—The method is based on the pptn. of dicarboxylic acids from the hydrolysed protein with $Ca(OH)_2$ and EtOH. Vals. obtained with several proteins are in close agreement with those obtained by direct isolation of the acids by other workers. The N distribution in protamine from Ragi has been determined. S. S. Zilva.

Occurrence of methylated nitrogen compounds in sea-weed. II. Administration of trimethylamine to cold-blooded animals. R. Kapeller-Adler and F. Vering (Biochem. Z., 1931, 243, 292—309 ; A., 1930, 1464, 1484).—Neither marine nor fresh-water plants contain $NHMe_2$ and only the former contain NMe_3, whilst both contain NH_2Me. There is no NMe_3 oxide in marine plants. The NH_3 content of both species varies very widely. Except for *Elodea canadensis*, which contains 0·03% of NH_2Me, other fresh-water plants contain 0·0015—0·004%. Green and brown marine algæ contain 0·01—0·044% and 0·05% of NMe_3, respectively. In red marine algæ the NMe_3 content varies greatly (0·017—0·5%) from species to species ; the NH_2Me content of these algæ is 0·014—0·08%. In the marine plants there is no connexion between botanical relationship and content of methylated amine. When NMe_3,HCl is fed to goldfish small amounts of the substance (but no NMe_3 oxide) are deposited in their musculature, and it is concluded that the methylated amines and NMe_3 oxide found in sea fish may be derived from their food. W. McCartney.

Wood saps. I. Sap of the red beech (*Fagus sylvatica*). C. G. Schwalbe and W. Ender (Cellulosechem., 1931, 12, 316—318).—The sap in the capillaries of the red beech contains considerable amounts of carbohydrates (chiefly hexoses and some pentoses), K, Na, Ca (17·4% of the ash), Mg (9·2%), Cl (6·12%), PO_4, and org. acids (probably lactic acid). N is absent. The carbohydrates are considered as hygroscopic substances responsible for the changes in the wood with varying humidity. R. S. Cahn.

Toxicity of water-soluble extractives of Western Yellow Pine to *Lenzites sepiaria*. B. A. Anderson (Phytopath., 1931, 21, 927—940).—Hot-H_2O extracts were more toxic than cold, and those from air-seasoned wood more toxic than from kiln-dried. A. G. Pollard.

Permeability of *Rhoeo* cells to ammonia and acetic acid. R. Collander, O. Turpeinen, and E. Fabritius (Protoplasma, 1931, 13, 348—362).—The permeability of epidermal protoplasts of leaves of *R. discolor* to NH_4OAc is controlled by the degree of dissociation of the salt solution, the rate of penetration of undissociated mols. being very small. A. G. Pollard.

Influence of the potassium : nitrogen ratio on the early growth of the coffee plant. T. de Camargo (Compt. rend., 1931, 193, 1032—1034).—The growth of young *Coffea arabica*, L., plants is greatest when the culture solution has a $K_2O:N$ ratio of 1, the contents of protein, sucrose, starch, and cellulose of the leaves also showing a max., whilst those of glucose and methylpentoses increase with decreasing vals. of the ratio. F. O. Howitt.

Histological basis of the effect of potash on the "lodging" of barley. C. Blattny and V. Vukolov (Ernähr. Pflanze, 1931, 27, 355—358).—Changes in the tissue structure of barley straw, especially of the nodes, resulting from K manuring are described. A. G. Pollard.

Can potash and nitrogen deficiencies be determined by chemical tests of parts of living plants ? W. Kruger, G. Wimmer, and H. Lüdecke (Ernähr. Pflanze, 1931, 27, 425—429, 450—452).—The Hoffer method for detecting K deficiency by means of Fe accumulation at the nodes of maize stems (Washington Agric. Exp. Sta. Bull., 1926, No. 298) gave uncertain results for maize and was inapplicable to oats. Individual plants show considerable variation and climatic conditions affect results. Applications of the $NHPh_2$ test for NO_3' in freshly-cut plant stems does not give a satisfactory indication of N deficiency. A. G. POLLARD.

Micro-detection of phosphorus in plant cells. B. ANGELI (Riv. Biol., 1928, **10**, 6 pp.; Chem. Zentr., 1931, ii, 95).—Sections are immersed for 20 min. in a $HCl-(NH_4)_2MoO_4$ solution, rapidly washed, immersed in freshly prepared $0{\cdot}02N$-$SnCl_2$, washed with H_2O, and moistened with 2·5% aq. NH_3. Where P is present a blue colour is observed under the microscope. A. A. ELDRIDGE.

Manganese and the growth of *Lemna minor*. E. F. HOPKINS (Science, 1931, **74**, 551—552).—Mn is confirmed to be essential for the growth of *Chlorella* (A., 1931, 400). With or without Fe or glucose, it is also essential for the growth of *L. minor*.

L. S. THEOBALD.

Bromine normally present in plants: edible grains, wheat, and bread. A. DAMIENS and S. BLAIGNAN (Compt. rend., 1931, **193**, 1460—1462).—The ratio Br/Cl has been determined in various grains, including rice, peas, beans, wheat, and other cereals and also in flour, bread, and yeast. In rice and haricot beans only traces of the halogens were found.

W. O. KERMACK.

Distribution of iodine in grain. E. GLIMM and S. HALASA (Biochem. Z., 1931, **243**, 88—96).—The I contents of the seed and the whole plant are determined for a number of cereals (rye, wheat, barley, oats, maize). The I distribution within the grain is not uniform, the content being greatest at the top and least in the middle portion. The abs. I content of the whole plant is distributed fairly evenly between stalk, root, and ear, and relatively is poorest in the ear and richest in the root. Malt is always poorer in I than the barley from which it is obtained.

P. W. CLUTTERBUCK.

Inorganic constituents of the several parts of *Monarda fistulosa*. E. KREMERS and A. A. HARWOOD (J. Amer. Pharm. Assoc., 1931, **20**, 1268—1272; cf. B., 1931, 945).—Analyses of the ash of the root, stem, leaf, bract, and corolla are given.

E. H. SHARPLES.

Effects of calcium deficiency on nitrate absorption and on metabolism in tomato. G. T. NIGHTINGALE, R. M. ADDOMS, W. R. ROBBINS, and L. G. SCHEMMERHORN (Plant Physiol., 1931, **6**, 605—630).—Ca-deficient tomatoes are characterised by the yellowing of the upper stems and leaves (lower portions remaining green) and by short bulbous roots, brown at the tips with sloughing-off of cells further back. The latter is attributed in part to lack of development of the middle lamella of Ca pectate. Deficiency of Ca results in a lack of ability to assimilate nitrates. The plants accumulate considerable amounts of carbohydrates, but the translocation of sugars and the digestion of starch proceed freely. Nearly all the Ca present in deficient plants is insol. in H_2O and is located chiefly in the older tissues of roots and tops. A portion of this Ca is present as oxalate, but the major part ("combined Ca") occurred in other forms which react with $H_2C_2O_4$ only after treatment with alkali. Both forms of Ca were so slowly utilisable that normal maintenance of tissues was impossible. New cell formation necessitates sufficient Ca to form the middle lamella and for combination with the materials of the protoplast. In its absence granular proteinaceous inclusions accumulate.

A. G. POLLARD.

Reaction of substrate of *Rumex acetosella*. E. KIVINEN (J. Sci. Agric. Soc. Finland, 1931, 10—16; Proc. Internat. Soc. Soil Sci., 1931, **6**, 125—126).—The range of p_H of soils in which *R. acetosella* occurs varies with soil type and in general was lower in cultivated than in uncultivated areas. Average vals. were: peats, p_H 4·76; silts, 5·01; sands, 5·7; gravels, 6·10. A. G. POLLARD.

Freezing-point depressions of asparagus shoots determined by a thermo-electric method. E. I. FERNALD (Contr. Boyce Thompson Inst., 1931, **3**, 483—497).—Use of a Cu-constantan thermocouple is described. Max. f.-p. depressions of sections of actively growing asparagus shoots occurred at distances of 1 and 3 cm. from the tip when underground and 1·5—3·7 cm. when above ground.

A. G. POLLARD.

Influence of protoplasm rotation on the transport of substances. A. C. A. KOK (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 918—929).—The diffusion of Li salts and of caffeine through the leaves of *Vallisneria spiralis* is hindered by the protoplasm the rotation of the granules of which is without influence on the rate of transport. Et_2O retards the transport to a small extent, not due to inhibition of rotation, but to decrease in permeability of the protoplasm. 0·0001% $CuSO_4$ used for the initiation of the rotation in leaves in which protoplasmic movement has ceased following removal from light causes either no change or only a slight increase in the transport velocity. Rise in temp. accelerates the diffusion, the temp. coeff. being 1·4.

F. O. HOWITT.

Periodic permeability of iodine solution and of water in the protoplasm of *Zea mais* seeds. R. C. MALHOTRA (Protoplasma, 1931, **13**, 374—388).—The rate of intake of H_2O and of 0·05% I solution by maize seeds increases with time of contact and with rise of temp. The actual intake of H_2O was greater from the I solution than from distilled H_2O. Germination of seeds treated with I solution at 25° was normal and seedlings made slightly better growth than controls. No stimulation resulted from I treatment at higher temp. A. G. POLLARD.

Relation between seeds and micro-organisms. T. R. SATHE and V. SUBRAHMANYAN (J. Indian Inst. Sci., 1931, **14A**, 119—139).—There is no direct evidence of the presence of living micro-organisms inside healthy seeds. The micro-organisms usually found on the seed-coat are derived from the soil and are physiologically unrelated to the seed. Treatment of the seed-coat with antiseptic material is not inimical to germination or to the development of the seedling provided the material is removed prior to sowing. W. G. EGGLETON.

Vital staining of plant cells with erythrosin. S. STRUGGER (Ber. deut. bot. Ges., 1931, **49**, 453—476).—The visible effect of plasmolysing erythrosin-stained cells from the epidermis of *Allium cepa* and the root hairs of *Hydromystria bogotensis* with aq.

KNO_3 is described. Such staining increases at first the permeability of the cell membrane; the cytoplasm, however, soon ceases to swell, and finally coagulation of the protoplasts takes place. Vital staining occurs up to the point when the nucleus becomes irreversible. A. Lawson.

Loss of glucose from dried peas on soaking. W. M. Clifford (Biochem. J., 1931, **25**, 1999—2003).—Dried peas lose 0·1—0·15% of glucose on soaking in distilled H_2O for 18—24 hr. The loss is greater after the addition of acids, especially org. acids, but not of alkalis. The uptake of H_2O by dried peas is depressed by the addition of acids, alkalis, or salts. The rate of cooking of peas is unaltered by previously soaking them in acids, alkalis, or salts unless the concn. of alkali or salt is high enough to soften the whole pea in the cold. Such concn. renders the pea inedible. S. S. Zilva.

Variations in the Evening Primrose induced by radium. W. H. Brittingham (Science, 1931, **74**, 463—464). L. S. Theobald.

Toxic action. II. Toxicity of normal aliphatic alcohols towards potato. III. Parallelism between surface activity and toxicity of normal aliphatic alcohols. W. Stiles and M. L. L. Stirk (Protoplasma, 1931, **13**, 1—20, 363—373).—II. The toxicity to potato tuber of aliphatic alcohols as determined by the rate of exosmosis of electrolytes into solutions of the alcohols (cf. *ibid.*, 1927, **2**, 577—601) increased with the no. of C atoms in the chain. In the series MeOH to octyl alcohol, addition of 1 C atom increased the toxicity 2·5—4·7 times.

III. In Traube's law concerning the surface tension of solutions of alcohols the factor 3 is approx. only, the average val. for 8 alcohols examined being 3·3. Equi-toxic solutions of different alcohols do not necessarily possess the same surface tension. Surface tension and toxicity increased with mol. wt., but the rise in surface tension was relatively more rapid than that of toxicity. A. G. Pollard.

Effect of heavy-metal compounds on plant cells. A. Niethammer (Bot. Archiv, 1931, **33**, 41—47).—The effect of solutions of salts of Ni, Hg, Cu, Zn, Co, and Al on the plasmolysis of epidermal leaf cells and of seeds is recorded. Prolonged contact with Hg salts causes the emergence of the plasma and nucleus from cells. A. G. Pollard.

Rust-resistance in wheat. V. Physiology of the host. W. F. Hanna (Canadian J. Res., 1931, **4**, 134—147).—Catalase activity increases and diastase activity decreases as the plant matures. The oxidase activity and the rates of respiration of the 8 varieties do not differ. The wheats most susceptible to stem rust are those richest in chlorophyll, xanthophyll, and carotene. Photosynthetic processes may take place rapidly and furnish conditions suitable for the growth of the rust mycelium. A. Renfrew.

Immunological studies on press juice and pigments of leaves. H. Hodyo (J. Biochem., Japan, 1931, **13**, 273—289).—Sp. immune bodies are formed when rabbits and guinea-pigs are immunised by applications to the skin of the press juice or pigments of leaves mixed with lanolin. Leaves from closely related species can be differentiated, but results with chlorophyll were uncertain. Chemical Abstracts.

Serological analysis of protein complexes (protenoms) as a method of investigating biological relationships. O. Moritz (Ber. deut. bot. Ges., 1931, **49**, 76—78).—A discussion of the application of immunological methods for the detection of biological relationships. W. O. Kermack.

Determination of reducing sugar in syrups, blood, cerebrospinal fluid, milk, and urine. T. Ugarte (Anal. Assoc. Quím. Argentina, 1931, **19**, 137—161).—The fluid for analysis is added, until the blue colour disappears, to 1 c.c. of a boiling solution prepared by adding NaOH to $CuSO_4$ in aq. glycerol. 1 c.c. of reagent containing 0·7% of $CuSO_4,5H_2O$, 4% of glycerol, and 2% of NaOH is equiv. to 1 mg. of glucose; 1 c.c. containing 0·07% $CuSO_4,5H_2O$, 4% of glycerol, and 0·4% of NaOH is equiv. to 0·1 mg. of glucose. The details of the determination of sucrose after inversion and of glucose in physiological fluids are described. The accuracy is comparable with that of the Hagedorn–Jensen method. R. K. Callow.

Naphtharesorcinol reaction of alduronic acids. C. Neuberg and M. Kobel (Biochem. Z., 1931, **243**, 435—450).—In carrying out the reaction 2*N*-HCl or 50% H_2SO_4 should be used as condensing agent and the mixture heated at 100°. The dye then separates in flocculent form and is best extracted with $CHCl_3$ or C_6H_6 (AcOEt, PhMe, or Et_2O can also be used). Glucose, galactose, mannose, xylose, arabinose, maltose, and lactose in ratios not greater than 200 parts to 1 part of uronic acid, fructose in ratios not exceeding 40 : 1 (for galacturonic acid) or 30 : 1 (for glycuronic acid), or sucrose in ratios not exceeding 50 : 1 do not interfere. Simply combined uronic acids (*e.g.*, those in urine) react directly, since they are hydrolysed by the acid used, but the more complex ones must first be hydrolysed with *N*-H_2SO_4. If material containing carbohydrates capable of fermenting fails, after fermentation, to react with naphtharesorcinol, but then reacts when a trace of uronate is added, uronic acids are absent. A method of preparing galacturonic acid from orange rind is given. W. McCartney.

Determination of cystine in proteins by the method of Folin and Marenzi. S. L. Tompsett (Biochem. J., 1931, **25**, 2014—2016).—A solution of $NaHCO_3$ is used instead of that of Na_2CO_3. The colour produced in the presence of the former is uninfluenced by its concn. and no turbidity occurs. The cystine content of gelatin, caseinogen, edestin, ovalbumin, and serum-albumin has been determined. S. S. Zilva.