

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JULY, 1934.

General, Physical, and Inorganic Chemistry

Width of spectral lines in gases. V. WEISSKOPF (Uspekhi. Fiz. Nauk., 1933, 13, 552—592).—Widths of the Hg line 2537 Å. and the Na *D* lines in H₂, He, A, Ne, N₂, O₂, CO₂, and CO have been measured. CH. ABS.

Fine structure of the triplets $(2s^2)(2p)3s^3\phi \rightarrow (2s^2)(2p^3)^3\phi$ of the carbon atom. V. M. TSCHULAKOVSKI and M. P. MOCHNATKIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 18—20).—The structure of the triplets in the neighbourhood of 1656 Å. has been investigated. A. J. M.

Spectral intensities by comparison with total radiation. T. N. PANAY (J. Phys. Radium, 1934, [vii], 5, 171—178).—For the comparative measurement of spectral intensities a black body formed by an electrically heated C tube in A is described. Black bodies of const. temp. have been prepared by the spherical end of a quartz tube in boiling Zn surrounded by N₂, and by C in boiling Pb surrounded by A. N. M. B.

Intensity distributions in molecular spectra: N₂ second positive system. N. R. TAWDE (Proc. Physical Soc., 1934, 46, 324—332).—Intensities of bands in the C³Π → B³Π system of N₂ under four different conditions of excitation were measured by means of calibrated photographs. N. M. B.

Effective rotation temperature of the negative glow in nitrogen. N. THOMPSON (Proc. Physical Soc., 1934, 46, 436—443).—The effective rotation temp. was determined from the intensity distribution in the (0,0) band of the N₂ negative system under varying conditions of excitation, using specially designed discharge tubes. The effective temp. increases slightly with pressure and current strength and to a much greater extent with the temp. of the furnace surrounding the tube; ultimately it becomes < the temp. of the furnace. This anomaly is not explained. N. M. B.

Intensity measurements in the first positive bands of nitrogen. A. ELLIOTT and W. H. B. CAMERON (Nature, 1934, 133, 723). L. S. T.

Hyperfine structure of fluorine. F. W. BROWN and J. H. BARTLETT, jun. (Physical Rev., 1934, [ii], 45, 527—537).—Mathematical. Application of the theory of Breit (cf. A., 1931, 275) gives multiplet structures in good agreement with experiment. N. M. B.

Presence of forbidden lines of Ne v in nebular spectra. P. SWINGS and B. EDLÉN (Compt. rend., 1934, 198, 1748—1750).—The nebular lines (I),

λλ 3346 and 3426, are attributed to the forbidden transitions $^3P_2 \rightarrow ^1D_2$ and $^3P_1 \rightarrow ^1D_2$ of Ne v, in agreement with calc. λλ and intensities. (I) are emitted from the central regions of nebulae. B. W. B.

Optical constants of alkali metals. J. HURGIN and N. PISARENKO (Nature, 1934, 133, 690). L. S. T.

Mechanism of glow discharge in the positive column of argon. O. GROOS (Z. Physik, 1934, 88, 741—756).—Measurements are given of the longitudinal field, density of carriers, wall current, and electron temp. to a pressure of 10⁻⁴ tor, and an explanation is given of the dependence of gradients on mean free path. A. B. D. C.

Hyperfine structure of the green krypton line 5570 Å. M. ROMANOVA and A. FERCHMIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 546—548).—At liquid air temp. the hyperfine structure of the 5570 Å. Kr line shows eleven components, the separations of which are in agreement with the term scheme suggested by Kopfermann and Wieth-Knudsen (A., 1933, 1095). J. W. S.

Pressure broadening and displacement of the fourth term of the caesium principal series. F. GÖSSLER and H. E. KUNDT (Z. Physik, 1934, 89, 63—67).—Lack of symmetry, half-width val., and displacement due to presence of He, Ne, A, and N₂ were observed for the 3612 Å. Cs line. A. B. D. C.

Self-energy of the electron. V. WEISSKOPF (Z. Physik, 1934, 89, 27—39).—Theoretical. A. B. D. C.

Action of a stream of slow electrons on the plasma of the mercury arc. S. GVOZDOVER and F. KONOVALOV (Compt. rend., Acad. Sci. U.R.S.S., 1934, 1, 553—557). J. W. S.

Anomalous intensity increase of the 5461 Å. mercury line in the N₂ + O₂ discharge. N. PRILESHAJEWA (Z. Physik, 1934, 89, 24—26).—A phenomenon similar to that observed by Günther-Schulze and Betz (A., 1933, 992) is recorded. A. B. D. C.

Temperature radiation in spark discharges? W. FINKELNBURG (Z. Physik, 1934, 88, 763—767).—The continuous spark spectrum is not temp. radiation (cf. Rathenau, this vol., 129). A. B. D. C.

Continuous electron radiation in spark discharges. W. FINKELNBURG (Z. Physik, 1934, 88, 768—778).—All spark discharges in liquids and gases

show similar continuous spectra due to continuous electron radiation. A. B. D. C.

Spectral intensity distribution of night sky and Northern lights. L. VEGARD and E. TÖNSBERG (*Z. Physik*, 1934, **88**, 709—726).—A comparison of the intensity of the various lines of the two spectra is given, and night sky light is shown to be due to active N_2 and to O_2 activated by the N_2 . A. B. D. C.

Spectroscopy of ultra-soft X-rays. III. M. SIEGBAHN and T. MAGNUSSON (*Z. Physik*, 1934, **88**, 559—592; cf. this vol., 232).— M and N series are given for wave-lengths between 20 and 500 Å. A. B. D. C.

Transitions to optical levels in the argon L X-ray absorption spectrum. J. A. PRINS (*Nature*, 1934, **133**, 795—796). L. S. T.

Faint lines in the L spectrum of the elements 73 Ta to 83 Bi. II. S. KAUFMAN (*Physical Rev.*, 1934, [ii], **45**, 613—616; cf. this vol., 577).—Data for additional faint diagram and non-diagram lines in the $L\gamma$ region of the X-ray spectra, for three new non-diagram (satellite) lines associated with $L\gamma_1$ and $L\gamma_2$, for the close pair Pb $L\beta_1$ and Pb $L\beta_2$, and for the strong lines of Os in the $L\beta$ and $L\gamma$ regions are given. N. M. B.

Extension of the dynamic theory of X-ray interference. L. POSENER (*Ann. Physik*, 1934, [v], **19**, 849—877).—Mathematical. A. J. M.

Inner potential of crystals. S. KIKUCHI and S. NAKAGAWA (*Z. Physik*, 1934, **88**, 757—762).—Lower-order reflexions of cathode rays give lower vals. of inner potential than the higher orders, possibly due to lack of definition of inner potential at grazing incidence. A. B. D. C.

Discharge rays. A. DAUVILLIER (*J. Phys. Radium*, 1934, [vii], **5**, 184).—Explanations of Rebooul's "discharge rays" (cf. A., 1933, 442) are discussed. N. M. B.

Gamma-ray ionisation in several gases as a function of pressure and collecting field. E. F. COX (*Physical Rev.*, 1934, [ii], **45**, 503—506).—Data for ionisation by low-intensity γ -radiation in N_2 , CO_2 , A, and He over a wide range of pressures and collecting fields discredit Broxon's wall emission theory (cf. A., 1932, 3) and favour a recombination theory. N. M. B.

Photo-electric effect for high energy quanta. H. HALL (*Physical Rev.*, 1934, [ii], **45**, 620—627; cf. A., 1931, 1105).—Mathematical. The cross-section for photo-electric absorption of a Dirac electron in the field of a nucleus is calc. for the case of quantum energies $h\nu >$ the proper energy mc^2 of the electron. N. M. B.

Thoriated tungsten filaments. I. LANGMUIR (*J. Franklin Inst.*, 1934, **217**, 543—569).—From new relations between v_e , the rate of evaporation of electrons from a thoriated W filament, and θ , the fraction of the surface covered by Th atoms, a recalculation of available experimental data gives results for v_a , the atom evaporation rate, as a function of θ and temp. T in good agreement with the vals. of v_a calc. from v_e . The diffusion coeffs. of Th through W crystals, along grain boundaries, and over the free filament surface,

are calc. A theory of the variation of the surface diffusion coeff. with the no. of Th atoms per sq. cm. is given. The probable mechanism of the production of Th within the filament is discussed (cf. Brattain, A., 1933, 441). N. M. B.

Thermionic cathodes. C. G. FOUND (*Physical Rev.*, 1934, [ii], **45**, 519—526).—From the relation between the electron current from a thermionic cathode and the positive ion current two new methods of determining the thermionic emission of a cathode in a gaseous discharge are described. Zero field emission of an oxide-coated cathode is only about 10% of the normal operating current. Emission increases linearly with field up to 150 volts per cm. Total ionising power increases linearly with the accelerating potential of the electron for voltages up to two or three times the resonance potential. N. M. B.

Apparent thermionic constant A of clean metals. A. L. REIMANN (*Nature*, 1934, **133**, 833). L. S. T.

Magnetic refocussing of electron paths. W. E. STEPHENS (*Physical Rev.*, 1934, [ii], **45**, 513—518).—A general method of refocussing slightly divergent electron paths in a uniform magnetic field is described. N. M. B.

Electron spin. J. SOLOMON (*J. Phys. Radium*, 1934, [vii], **5**, 167—170).—The possibility of obtaining experimentally a beam of electrons completely polarised, or with parallel spin, is discussed. N. M. B.

Resonance conditions and acceleration of electrons according to Bloch's theory of electrical conductivity. E. KRETSCHMANN (*Z. Physik*, 1934, **88**, 792—799).—Polemical, against Peierls (cf. this vol., 721). A. B. D. C.

Small-angle scattering of electrons in helium. F. C. POULTNEY and R. WHIDDINGTON (*Nature*, 1934, **133**, 685). L. S. T.

Paramagnetism of electron gas. H. OSTERMANN (*Z. Physik*, 1934, **89**, 68—82).—A paramagnetic electron gas should give a charge current. A. B. D. C.

Polarisation of electrons. G. P. THOMSON (*Phil. Mag.*, 1934, [vii], **17**, 1058—1071; cf. this vol., 126).—Polarisation experiments in which electrons are scattered at right angles and then diffracted by a thin film, and in the second case are scattered twice at right angles, show no asymmetry. Voltages were 153 in the first case, and 30 and 103 kv. in the second case, the last two being contrary to Dirac's theory of the electron. N. M. B.

Statistics of positrons and electrons in equilibrium with radiation at high temperatures. G. WATAGHIN (*Phil. Mag.*, 1934, [vii], **17**, 910—913).—Mathematical. N. M. B.

Radiation originating in collisions of fast electrons. C. F. VON WEIZSÄCKER (*Z. Physik*, 1934, **88**, 612—625).—Two cases, that of ordinary scattering, and that of transformation of a very high energy photon into a negative and positive electron, are treated theoretically. A. B. D. C.

Multiple acceleration of ions to very high speeds. E. O. LAWRENCE and M. S. LIVINGSTON

(Physical Rev., 1934, [ii], 45, 608—612).—An enlarged form of an apparatus previously described (cf. A., 1932, 554) is capable of generating H ions with energies up to 5×10^6 volt electrons, for use in nuclear research. At 3×10^6 volts ion currents of 0.3 microamp. are obtained.

N. M. B.

Deuteron and disintegration. H. J. WALKE (Phil. Mag., 1934, [vii], 17, 1023—1024; cf. this vol., 471).—An alternative explanation of the new type of positron emission (cf. Curie, this vol., 234) is discussed.

N. M. B.

Fourth Report of the Committee of Atomic Weights of the International Union of Chemistry. G. P. BAXTER, (MME.) P. CURIE, O. HÖNIGSCHMID, P. LEBEAU, and R. J. MEYER (J.C.S., 1934, 499—512, J. Amer. Chem. Soc., 1934, 56, 753—764, and Ber., 1934, 67, [A], 47—67).—The following alterations are recommended: K=39.096; As=74.91; Se=78.96; In=114.76; Te=126.61; Cs=132.91; Yt=173.04; Os=191.5.

H. W.

Revision of the at. wt. of caesium. G. P. BAXTER and J. S. THOMAS (J. Amer. Chem. Soc., 1934, 56, 1108—1110).—From the ratio CsCl : Ag the at. wt. of Cs is 132.91.

E. S. H.

Constitution of hafnium and other elements. F. W. ASTON (Nature, 1934, 133, 684).—The mass spectrum of Hf indicates five isotopes, a weak line at 176 and strong lines at 177, 178, 179, and 180, with the even nos. somewhat more abundant. Th appears to be simple 232. Rh gives the feeblest effect of any element analysed, with only one line at 103 clearly detectable. Intense spectra from Ca showed new isotopes 42 and 43 in addition to 40 and 44 discovered by Dempster. A line at 41 may probably be due in part to another Ca isotope. The main line 48 of Ti is accompanied by faint lines at 46, 47, 49, and 50, the whole forming a symmetrical group. Zr has an additional and fairly abundant isotope 91, and the presence of isotope 96 is now confirmed. Sm has two faint isotopes 144 and 150. Pd, Ir, Pt, and Au still give negative results.

L. S. T.

Research on heavy hydrogen at Princeton. H. S. TAYLOR (Science, 1934, 79, 303—305).—A summary.

L. S. T.

Two kinds of H₃. (SIR) J. J. THOMSON (Phil. Mag., 1934, [vii], 17, 1025—1030).—Bombardment of certain solids by cathode rays gives a permanent gas H₃, and a discharge through normal H₂ gives a H₃ of very short life. Photographs of parabolas and positive-ray analysis show that the permanent H₃ obtained by a discharge in normal H₂ is $< 1/8500$ of the normal H₂, and that permanent H₃ obtained by bombarding KOH was, in two samples, $1/720$ and $1/480$ of the normal H₂. In the photographic method the effects due to the short-lived and permanent forms of H₃ are superposed, but in the electrical method the effect of the fugitive H₃ is eliminated. Parabolas for H₂, H₃, and H₄ for a specimen containing 80% H₂ are of approx. the same intensity and correspond with the electrical effects due to these lines.

N. M. B.

Field combinations in velocity and mass-spectrography. II. W. HENNEBERG (Ann. Physik, 1934, [v], 20, 1—12; cf. this vol., 341).—Mathe-

matical. Use can be made of the large dispersion in the equatorial plane of a magnetic dipole field for spectroscopic purposes. For focussing, an electron lens may be used, or a homogeneous magnetic field and the field of a cylindrical condenser may be superposed.

A. J. M.

Periodic law and its interpretation. (LORD) RUTHERFORD (J.C.S., 1934, 635—642).—Mendeléef Centenary Lecture.

J. W. S.

At. wts. and isotopes. E. C. FRITZMAN (J. Appl. Chem. Russ., 1934, 7, 279—296).—A review.

R. T.

Anomalous thermal activity of radioactive minerals. A. SANIÉLÉVICI (J. Chim. phys., 1934, 31, 192—196).—The abnormal evolution of heat at a const. rate by orangeite is attributed to adsorption of H₂O and hydration, since the mineral in a sealed vessel gradually loses its anomalous thermal activity.

J. G. A. G.

Mobility of polonium on and in silver. K. SCHWARZ (Z. physikal. Chem., 1934, 168, 241—247).—There is "vaporisation" of Po from a Ag surface even at comparatively low temp. The interpretation of this phenomenon as due to aggregate recoil (cf. A., 1920, ii, 656) agrees with the observation that the rate is independent of the temp. at 100—350°. Thermal evaporation first becomes perceptible at 350—400°. Diffusion over the Ag surface begins to be detectable at 300° and increases with rise in temp. There is no measurable vol. diffusion into the Ag up to 500°.

R. C.

Radioactive elements of F. Joliot and I. Curie. G. C. WICK (Atti R. Accad. Lincei, 1934, [vi], 19, 319—324).—Theoretical.

O. J. W.

Half-life of actinouranium. F. WESTERN and A. E. RUARK (Physical Rev., 1934, [ii], 45, 628—629; cf. A., 1933, 1224; this vol., 234).—Calc. half life vals. for Ac-U from various sources are 3.38×10^8 and 4.45×10^8 years, based on branching ratios 0.03 and 0.04, respectively.

N. M. B.

Properties of samarium radiation. M. MÄDER (Z. Physik, 1934, 88, 601—611).— α -Rays of 1.16 cm. and H -rays of 1.37 cm. in air were observed.

A. B. D. C.

Magnetic spectrum of β -rays emitted by Th-B+C+C'+C''. R. ARNOULT (Compt. rend., 1934, 198, 1603—1605; cf. this vol., 470).—Similarities between Th and Ra(-B \rightarrow C) spectra suggest that the former is due to electronic reorganisation of atom 83 after ionisation of K levels by a γ -quantum. Nuclear levels are indicated for Th-B at 113.4, 236.7, and 411 ekv.

B. W. B.

β -Radioactivity. D. D. IVANENKO (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 537—539).—Theoretical.

J. W. S.

β -Emission of positive electrons. G. BECK and K. SITTE (Nature, 1934, 133, 722).—Theoretical.

L. S. T.

Secondary radiation of hard γ -radiation. W. BOTHE and W. HORN (Z. Physik, 1934, 88, 683—698; cf. this vol., 342).

A. B. D. C.

Artificial production of radioactive elements. Chemical proof of transmutation of elements.

(MME.) I. CURIE and F. JOLIOT (*J. Phys. Radium*, 1934, [vii], 5, 153—156; cf. A., 1933, 1224; this vol., 234, 343, 470).—B, Mg, and Al after irradiation by Po α -rays show radioactivity. B and Al emit positrons of max. energy 1.5×10^6 and 3×10^6 ev., respectively. Mg emits electrons and positrons forming two continuous spectra corresponding with the transmutation of two Mg isotopes. The decay of the three radio-elements created by transmutation is exponential, the half-decay periods being: B 14 min., Mg 2.5 min., Al 3.25 min., independent of the energy of the exciting α -rays. The new radioactive elements are probably the nuclei ${}^7\text{N}^{13}$, ${}^{14}\text{Si}^{27}$, ${}^{13}\text{Al}^{28}$, ${}^{15}\text{P}^{30}$, formed from ${}^5\text{B}^{10}$, ${}^{12}\text{Mg}^{24}$, ${}^{12}\text{Mg}^{25}$, and ${}^{13}\text{Al}^{27}$, respectively. The first chemical proof of artificial transmutation has been effected by the separation of the new elements, which show, from B and Al, the properties of N and P, respectively. N. M. B.

Induced radioactivity of sodium and phosphorus. O. R. FRISCH (*Nature*, 1934, 133, 721—722).—Na as NaCl, NaF, and $\text{Na}_2\text{C}_2\text{O}_4$ becomes active after α -ray bombardment, emitting chiefly positive electrons, with an initial activity approx. one half that of Al and half-val. period 7 ± 1 sec. Red P behaves similarly, the initial activity being approx. one sixth that of Al; half-val. period 40 ± 5 min. The range of the particles corresponds with an energy of 1.8×10^6 ev. Probable reactions are ${}^{11}\text{Na}^{23} + \alpha = {}^{13}\text{Al}^{26} + \text{neutron}$ and ${}^{15}\text{P}^{31} + \alpha = {}^{17}\text{Cl}^{34} + \text{neutron}$, and in the last case active Cl was separated. ${}^9\text{F}^{19}$ should show induced activity of very short life, but none was detected with CaF_2 . L. S. T.

Radioactivity induced by neutron bombardment. E. FERMI (*Nature*, 1934, 133, 757).—Bombardment by neutrons from Rn and Be induces strong radioactivity with P, Fe, Si, Al, Ag, I, and Cr; Cl, V, Cu, As, Te, Ba, and F also give definite effects, whilst indications of an effect are obtained with Na, Mg, Ti, Zr, Zn, Sr, Sb, Se, and Br. Some elements may give two or more periods. Active products, probably Si and Mn, respectively, have been separated in the case of P and Fe. The neutron appears to be absorbed and a proton emitted in these two cases. The unstable product, by emission of a β -particle, returns to the original element. L. S. T.

Induced radioactivity. H. J. WALKE (*Nature*, 1934, 133, 757—758).—Hypothetical. The radioactivity of the light elements is due to the formation within their nuclei of an unstable proton of excess energy which disintegrates by emitting a positron. L. S. T.

Collisions of neutrons with atomic nuclei. T. W. BONNER (*Physical Rev.*, 1934, [ii], 45, 601—607; cf. A., 1933, 762).—The target area of H, C, and N nuclei for neutrons obtained by the bombardment of Be, B, and F with Po α -particles increased with decrease of neutron velocity. The anomalous increase of absorption by Pb with velocity, as well as cosmic-ray bursts, can be explained by assuming that faster neutrons make relatively more inelastic collisions with the nuclei. The slower neutrons from F were more penetrating in Pb than those from Be or B. N. M. B.

Emission and scattering of neutrons. J. R. DUNNING (*Physical Rev.*, 1934, [ii], 45, 586—600).—Using high-intensity Be-Rn sources, the energy distribution of the neutrons emitted by bombardment of α -particles from Rn, Ra-A, and Ra-C' is analysed in terms of a no. of neutron groups, which are discussed in terms of transitions involving neutrons and γ -rays, with one or two resonance levels. The interaction of high-energy neutrons with matter appears to be mainly one of approx. elastic collisions with at. nuclei, resulting in neutron scattering. Data indicate for the neutron mass 1.0068, and radius 1.2×10^{-13} cm. approx. Nuclear radii cc (at. wt.)^{1/3}, approx., ranging from 2.5×10^{-13} for Li to 7.8×10^{-13} cm. for Pb. N. M. B.

Artificial production of neutrons. H. R. CRANE, C. C. LAURITSEN, and A. SOLTAN (*Physical Rev.*, 1934, [ii], 45, 507—512; cf. *ibid.*, 63; 1933, [ii], 44, 514, 692, 783).—The apparatus employed and results for Be and LiCl bombarded by deuterons, and Be bombarded by He ions, are described (cf. A., 1933, 1225). N. M. B.

Mass of the neutron. I. CURIE and F. JOLIOT (*Nature*, 1934, 133, 721).—The previous interpretation of the transmutation of B (A., 1933, 883) is confirmed by similar reactions observed with ${}^{13}\text{Al}^{27}$ and ${}^{12}\text{Mg}^{24}$. The reactions are ${}^5\text{B}^{10} + {}^2\text{He}^4 = {}^7\text{N}^{13} + {}^0\text{n}^1$ and ${}^7\text{N}^{13} = {}^6\text{C}^{13} + \epsilon^+$; ${}^{12}\text{Mg}^{24} + {}^2\text{He}^4 = {}^{14}\text{Si}^{27} + {}^0\text{n}^1$ and ${}^{14}\text{Si}^{27} = {}^{13}\text{Al}^{27} + \epsilon^+$; and ${}^{13}\text{Al}^{27} + {}^2\text{He}^4 = {}^{15}\text{P}^{30} + {}^0\text{n}^1$ and ${}^{15}\text{P}^{30} = {}^{14}\text{Si}^{30} + \epsilon^+$, where ${}^7\text{N}^{13}$, ${}^{14}\text{Si}^{27}$, and ${}^{15}\text{P}^{30}$ are unstable nuclei which disintegrate with the emission of positrons. From these equations and the energies involved calc. vals. for the mass of the neutron are 1.0098, 1.0092, and 1.0089 deduced from B, Al, and Mg, respectively, the first being the most exact. The val. adopted, 1.010 ± 0.0005 , gives 2.1×10^6 ev. for the energy liberated in the transformation neutron \rightarrow proton + ϵ^- and 3.1×10^6 ev. for that absorbed in the change proton \rightarrow neutron + ϵ^+ . L. S. T.

Observations of neutrons from cosmic radiation in a Wilson chamber. L. V. MISOVSKI and M. S. EIGENSON (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 2, 221—224).—Tracks of length 1 mm. to 15 cm., attributed to neutrons produced by cosmic radiation, were observed. H. J. E.

Neutrino. H. BETHE and R. PEIERLS (*Nature*, 1934, 133, 689—690).—Methods by which the existence of neutrinos could be experimentally tested are discussed. L. S. T.

Atomic disintegration by "non-capture." W. D. HARKINS and D. M. GANS (*Nature*, 1934, 133, 794).—Theoretical. At present there is no evidence that a nucleus has been disintegrated by a non-capture collision. L. S. T.

Progress of nuclear physics. E. HENRIOT (*Bull. Soc. chim. Belg.*, 1934, 43, 221—238).—A lecture.

Transmutation of elements. T. I. EFREMEENKO (*Ukrain. Chem. J.*, 1933, 8, 182—189).—Speculative. R. T.

Modern ideas on nuclear constitution. G. GAMOW (*Nature*, 1934, 133, 744—747). L. S. T.

Isomeric nuclei? G. GAMOW (Nature, 1934, 133, 833).—The line 210 in the mass spectrum of Pb indicates that the nucleus with at. no. 82 and at. wt. 210 may exist in two modifications, one of which is stable and the other subject to β -decay. L. S. T.

Constitution of cosmic rays. A. PICCARD (Compt. rend., 1934, 198, 1683—1685).—It is suggested that cosmic rays are primarily electromagnetic rays ($h\nu > 10^6$ ev.) which are almost completely absorbed by at. nuclei in the upper atm. with materialisation of electrons and positrons, the two latter mainly constituting the radiation observed at the earth's surface. B. W. B.

Residual ionisation by measurements with cosmic rays. B. GROSS (Ann. Acad. Brasil. Sci., 1934, 6, 1—10).—The residual ionisation can be obtained indirectly by making observations of the current intensity at two different depths. It can also be derived from an analysis of the absorption curve. A. J. M.

Coincidence counter studies of the corpuscular component of cosmic radiation. T. H. JOHNSON (Physical Rev., 1934, [ii], 45, 569—585). N. M. B.

Waves and photons. III. Dirac's approximation. A. PROCA (J. Phys. Radium, 1934, [vii], 5, 157—166; cf. this vol., 344, 580).—Mathematical. Associated with any light wave is a corpuscle of zero rest mass and for which the wave functions satisfy the Dirac relativistic equations. The corpuscle (neutrino) differs from a photon in its spin val. $h/4\pi$. The influence of the characteristics of the light on the states of the corpuscle is examined. The sign of its energy indicates the sense of rotation of the corresponding light, and gives an interpretation of negative energy states. N. M. B.

Anomalous dispersion in broad absorption bands. D. S. ROSHDESTVENSKI (Bull. Acad. Sci. U.R.S.S., 1934, 2, 35—57).—The anomalous dispersion of broad absorption bands arising from oscillators of fixed characteristic frequency and large damping const. differs from that of bands due to oscillators of variable characteristic frequency and small damping const., when observed by Puccianti's interference method. This method has been applied to the determination of the max. val. of the damping const. J. W. S.

Scattering of light in a medium of non-uniform temperature. L. I. MANDELSCHTAM (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 219—221).—Theoretical. H. J. E.

Resolution of crossed linking eigenfunctions in terms of the uncrossed set. H. EYRING and C. E. SUN (J. Chem. Physics, 1934, 2, 299—300).—Simplified rules are given. N. M. B.

Band spectrum of ionised aluminium hydride. W. HOLST (Z. Physik, 1934, 89, 40—49). A. B. D. C.

Isotope effect in the band spectrum of aluminium hydride. W. HOLST and E. HULTHÉN (Nature, 1934, 133, 796—797; cf. this vol., 472). L. S. T.

Significance of molecular absorption spectra. P. K. SEN-GUPTA (Z. Physik, 1934, 88, 647—660).—The discrepancy between the difference of limits of

continuous absorption and of corresponding at. levels is used to deduce the relative steepness of Franck-Condon curves for upper mol. levels, and is checked with the sharpness of absorption edges, and their wavelength variation with temp. Mols. discussed include N_2O , SO_3 , TeO_3 , MoO_3 , TeS_3 , P_2S_5 , HBr, HI, alkali halides, CdS, HgS, PbS, and ZnS. A. B. D. C.

Absorption spectra of ferric compounds. I. Ferric chloride-phenol reaction. E. F. WESP and W. R. BRODE (J. Amer. Chem. Soc., 1934, 56, 1037—1042).—The absorption spectra of aq. mixtures of PhOH with several Fe^{III} salts are identical in shape and position, but not in intensity. The absorption spectra of aq. mixtures of $FeCl_3$ with 44 phenols and 10 naphthols are identical in shape, but differ in intensity and position according to the nature and position of the substituent groups. Salicylic acid produces a colour with $FeCl_3$ only in solvents which are derivatives of H_2O or NH_3 . In 31 such solvents the absorption bands are identical in shape, but vary in position and intensity with the solvent. The Fe^{III} -PhOH colours appear to be due to the formation of complex co-ordinated ions of the type $(OR)_6^{III}$. E. S. H.

Change in light absorption due to hydrolysis and aggregation processes in alkaline and acid solutions of amphoteric hydroxides exemplified by iso- and hetero-polyvanadate solutions. K. F. JAHR and H. WITZMANN (Z. physikal. Chem., 1934, 168, 283—290).—The absorption curves of aq. Na vanadate solutions containing varying amounts of NaOH or $HClO_4$ demonstrate the existence of mono-, di-, tetra-, penta-, and octa-vanadic acids. The higher is the mol. wt. of the isopolyacid the flatter is the absorption curve and the further is absorption shifted towards longer waves. R. C.

Optical absorption of substituted benzenes. V. Xylene halides. H. CONRAD-BILLROTH (Z. physikal. Chem., 1934, B, 25, 217—224; cf. this vol., 582).—The ultra-violet absorption spectra of the xylene halides have been determined. Discrepancies between the observed positions of the bands and the positions calc. by the vector addition rule (A., 1933, 445) are perhaps a result of alternating polarity effects. In respect of fine structure and relative intensities of the partial bands there is considerable similarity between Cl- and Br-derivatives of the same geometrical structure. R. C.

Optical absorption curves of adsorbed *p*-nitrophenol molecules and their analysis. J. H. DE BOER and J. F. H. CUSTERS (Z. physikal. Chem., 1934, B, 25, 238—250).—Absorption curves have been determined at various stages of the adsorption by a vac.-sublimed CaF_2 surface. The curves can be resolved into two constituent curves, one corresponding with *p*-nitrophenol mols., the absorption spectrum of which has been shifted towards the red by electrostatic effects (α mols.), and the other with mols. optically unchanged by adsorption (β mols.). When adsorption commences, α mols. are adsorbed, and only when a certain no. of these have been adsorbed does the adsorption of β mols. start. In the final stages of adsorption it is chiefly β mols. which are taken up. The α mols. have their OH dipoles adsorbed on the F'

ions of the surface and the ring lying parallel to the surface, and are bound much more firmly than the β mols., which are held by van der Waals adsorption forces on the initial film of α mols., forming a second film. When the adsorption layer is complete it contains equal nos. of both kinds of mol. The displacement of the absorption spectrum of the α mols. is attributed to the weakening of the effect of the H' of the OH by the F' ion. R. C.

Spectroscopy of terpene alcohols and esters.—See this vol., 658.

Characteristic OH band in the near infra-red (about 0.96 μ). A. NAHERNIAC (Compt. rend., 1934, 198, 1685—1687).—Absorption spectra of vapours (I) of 14 monohydric alcohols were measured with a grating about 1 μ ; practically the only band found was that of OH, about 0.96 μ . The results compared with those of Freymann (A., 1933, 1228) for the liquids (II) show that the simple OH bands of (II) are more intense, slightly displaced towards shorter λ , and, with the exception of *tert.*-alcohols and phenols, are split into two components in (I). The influence of constitution on these phenomena is discussed. B. W. B.

Photography of the infra-red solar spectrum to wave-length 12,900 Å. G. HERZBERG (Nature, 1934, 133, 759).—The H₂O-vapour absorption band at 11,300 Å. has been resolved into its fine structure lines. An atm. O₂ band between 12,500 and 12,750 Å. is also discussed. L. S. T.

Far infra-red solar spectrum. J. DEVAUX (Compt. rend., 1934, 198, 1595—1596).—Absorption spectra were measured at Pic du Midi during Dec., 1933. Absorption in the 6—7 μ H₂O band was high, but not total. The intensity of the 10 μ O₃ band varied with the sun's altitude and was free from interference by H₂O. A new (possibly O₃) band at 7 μ is reported (cf. Gerhard, A., 1933, 208). B. W. B.

Infra-red absorption of water freshly prepared from ice and from steam. J. W. ELLIS and B. W. SORGE (Science, 1934, 79, 370—371).—Infra-red absorption spectra reveal no different concns. of poly-merides in H₂O freshly prepared from ice or steam. L. S. T.

Infra-red spectrum of methyl deuteride. E. F. BARKER and N. GINSBURG (J. Chem. Physics, 1934, 2, 299).—The replacement of one H in CH₄ by H² introduces a preferred axis, with respect to which the mol. is symmetrical, and increases the no. of active vibrations from two to six. These fundamental bands have been observed; the lowest frequency parallel vibration is at approx. 1090 cm.⁻¹, the interval between rotation lines being 4.5 cm.⁻¹, giving max. $I \sim 12.28 \times 10^{-40}$, and H—H distances 2.51×10^{-8} cm. N. M. B.

Raman effect, molecular refraction, and constitution. Supposed 1-benzylcyclohexene.—See this vol., 649.

Raman effect of seven normal alkyl nitrates. L. MÉDARD (J. Chim. phys., 1934, 31, 281—293).—Frequencies in the Raman spectra of RNO₃, where R is Me, Et, Prⁿ, Bus, *n*-amyl, *n*-C₆H₁₃, and *n*-C₇H₁₅, are tabulated. New lines have been found and others are shown to be doublets. The frequency due to the NO₃

ion does not occur in MeOH solutions of MeNO₃ (cf. Ganesan and Thatte, A., 1933, 114). The frequencies 1295 and 1679 cm.⁻¹ in 99.8% HNO₃ correspond with internal vibrations, comparatively little influenced by R, of the ·NO₂ group, whilst the frequency 612, related to the angle subtended by the two O atoms, decreases to 570 when R > Me. 860 (approx.) in RNO₃ increases to 922 in HNO₃ and is assigned to the O₂N·OR linking. The differences between the corresponding frequencies of the C chains decrease as R increases. Although the frequency at 2735 of alcohols is found, that at 2660 (I) does not occur in RNO₃, showing that (I) is not due to the C chain (cf. *ibid.*, 7). J. G. A. G.

Raman and infra-red spectra of the 1:2-dimethylcyclohexane stereoisomerides. J. LECOMTE, L. PIAUX, and O. MILLER (Bull. Soc. chim. Belg., 1934, 43, 239—242; cf. A., 1933, 998).—No absorption is shown in the ultra-violet. Infra-red absorption data are for the range 498—1450 cm.⁻¹ The bands 875—879 and 996—994 are common to the two forms. N. M. B.

Raman spectra of some compounds containing carbon-bromine linkings. Possible changes of the vibration frequencies in ionic solutions. H. E. VOGÉ (J. Chem. Physics, 1934, 2, 264—266).—Raman spectral data for CH₂Br·CO₂Me (liquid) and CHPhBr·CO₂Me in MeOH are tabulated. The C-Br linking of the former is similar to that for EtBr; in the latter it does not appear in its normal position. Revised data for MeOH and EtBr, and shifts of the CH₂Br·CO₂Me and MeOH lines in solutions of bromides, are given. N. M. B.

Raman effect and the benzene problem. J. WEILER (Z. Physik, 1934, 89, 58—62).—Observed infra-red and Raman fundamental frequencies agree not with hexagonal, but with trigonal, symmetry. A. B. D. C.

Action of electric discharge on phosphorescent substances. R. COUSTAL (Compt. rend., 1934, 198, 1596—1598; cf. this vol., 584).—Decay curves of phosphorescent sulphide screens (I) under- or over-excited by a brush discharge were photometrically compared with a normal (I) and shown to preserve const. intensity ratios throughout decay. It is suggested that two states of excitation of phosphorescent centres are involved. B. W. B.

Theory of phosphorescence. D. BLOCHINTZEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 79—81).—Mathematical. H. S. P.

New photo-electric effect in cuprous oxide. I. KIKOIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 73—76).—When a plate of Cu₂O at liquid air temp. is placed in a magnetic field and illuminated perpendicularly to the direction of the field, an e.m.f. perpendicular to both of these directions is produced. The current flowing depends on the intensity of the light and the strength of the field. Since the total conductance is the sum of the thermal and photo-effects, the e.m.f. tends to a limit with increasing intensity of illumination. H. S. P.

Oxide-coated photo-elements. I. G. LIANDRAT (J. Phys. Radium, 1934, [vii], 5, 179—183).—The inexactitude of theories of oxide-coated photo-

electric cells is attributed to neglect of the photo-conductivity effect in the oxide layer, which may, as in the "colour effect," be predominant. The impedance of a two-layer system in series is calc. and discussed.

N. M. B.

Relation between spectral sensitivity and absorption curves of dye photo-cells. (MLLE.) C. STORA (Compt. rend., 1934, 198, 1763—1765; cf. A., 1932, 898).—The displacements of max. of photo-electric sensitivity (*i.e.*, photo-current/incident energy) of dye/metal cells from the absorption max. of the dyes employed increased with the film-thickness of the dye. The seat of the photo-action was the thin film of dye immediately in contact with metal substrate.

B. W. B.

Determination of dipole moments by the molecular beam method. H. SCHEFFERS (Physikal. Z., 1934, 35, 425—433).—The dipole moments of KI, KCl, and NaI determined by the above method are 6.8×10^{-18} , 6.3×10^{-18} , and 4.9×10^{-18} e.s.u., respectively, thus agreeing with Debye's estimate.

A. J. M.

Dielectric constant of chemically defined substances. F. KELLER and W. R. LEHMANN (Z. Physik, 1934, 88, 677—682).—An attempt to measure dielectric consts. and relate them to the periodic system. Substances investigated include inorg. salts, oxides, and sulphides.

A. B. D. C.

Dipole induction effect in molecular compounds. Dipole moment measurements in molten naphthalene. G. BRIEGLEB and J. KAMBERTZ (Z. physikal. Chem., 1934, B, 25, 251—256).—A detailed account of work the principal results of which have already been published (this vol., 348).

R. C.

Temperature dependence of the relaxation time of polarisations in ice. E. J. MURPHY (Trans. Electrochem. Soc., 1934, 65, 309—318).—Determinations of dielectric const. of ice by a static method and by an a.c. method at frequencies from 16 to 10^5 cycles per sec. over a wide range of temp. indicate an exponential increase of the relaxation time of the polarised condition in the dielectric with fall of temp., from about 2×10^{-5} sec. at -0.8° to about 20 sec. at -139° . The nature of the polarisation responsible for the large dielectric const. of ice is discussed.

H. J. T. E.

Dielectric constants and transitions of solid ammonia, hydrogen sulphide, and methyl alcohol. C. P. SMYTH and C. S. HITCHCOCK (J. Amer. Chem. Soc., 1934, 56, 1084—1087).—The dielectric consts. of NH_3 , H_2S , and MeOH have been determined from 83° abs. to the m.p. No mol. rotation or transitions are observed in NH_3 , whilst two transitions are observed in H_2S , and one in MeOH. Mols. of H_2S appear to possess almost the same freedom of rotation as in the liquid state even when some degrees below the m.p.; with MeOH some freedom of mol. rotation exists in the narrow region between the m.p. and the transition point.

E. S. H.

Anomalous dispersion of the dielectric constant of Rochelle salt. G. BUSCH and P. SCHERRER (Helv. phys. Acta, 1933, 6, 234; Chem. Zentr., 1933, ii, 2794—2795).—Na K tartrate (I) shows an anomal-

ous dispersion of ϵ , at wave-lengths of a few thousand m., which is attributed to a piezoelectrical resonance of the crystals. ϵ for different sized plates of (I) has been measured for variable frequencies (10^4 — 5×10^5 Hertz) at 6 — 36° . The resonance wave-lengths and ϵ are max. at 22° .

L. S. T.

Dipole moments of liquids. R. F. GOSS (J.C.S., 1934, 696—699).—From the formula of Raman and Krishnan (cf. A., 1928, 348), relating electrical polarisation with anisotropy in the liquid state, a method has been developed for calculating the dipole moment (μ) from measurements on the pure liquid and on its dil. solutions. μ for MeCl and CHCl_3 are calc. from the data of Morgan and Lowry (A., 1931, 148) as 1.85 and 1.20×10^{-18} e.s.u., respectively.

J. W. S.

Dielectric properties of acetylenic compounds.

II. Electric moments of alkyl halogenoacetylenes. D. J. PFLAUM and H. H. WENZKE (J. Amer. Chem. Soc., 1934, 56, 1106—1107; cf. this vol., 585).—Measurements of dipole moments of α -chloro-, α -bromo-, and α -iodo- Δ^2 -hexinene and -heptinene show that the C-halogen linking decreases in polarity as the C becomes less saturated.

E. S. H.

Absorption measurements in liquids in the region of short electric waves. **III.** J. MALSCH (Ann. Physik, 1934, [v], 20, 33—56; cf. A., 1932, 470; this vol., 585).—An abs. method for the determination of refractive and absorption indices of liquids for waves of the order of 1 m. is described. Both consts. are determined simultaneously without alteration of the arrangement of the apparatus. The method was applied to $\text{Bu}^\alpha\text{OH}$ and Bu^βOH using 180-cm. waves. The behaviour of both substances in the range 50—5000 cm. can be explained quantitatively by the dipole theory of Debye.

A. J. M.

Anomalous dispersion in crystalline solids.

C. E. SUN and J. W. WILLIAMS (Trans. Electrochem. Soc., 1934, 65, 219—229).—Dielectric consts. of C_6H_6 , PhNO_2 , COPh_2 , COPhMe , and NH_3 in the cryst. state have been measured over a wide range of temp. and at frequencies from 1 to 600 kilocycles per sec. The significance of the results is discussed with special reference to the application of Debye's dipole theory.

H. J. T. E.

Ionising power of combinations of two partial [dipole] moments. A. E. VAN ARKEL and J. L. SNOEK (Rec. trav. chim., 1934, 53, 675—676; cf. A., 1933, 8).—The ionising power of a solvent is not determined solely by its dielectric const. (Walden's rule), as is shown by measurements of the conductivity of AcOH in C_6H_6 , *p*- and *o*- $\text{C}_6\text{H}_4\text{Cl}_2$, and PhCl. There is much less difference between the first two than between either of them and either of the last two. This indicates that the action of a single Cl-moment may be influenced by the existence in the ring of another such moment, and by its position.

F. L. U.

Explanation of transference of charge and electrophotophoresis on the ionic theory. A. LUSTIG and M. REISS (Physikal. Z., 1934, 35, 340—344).—The theory of Sitte (A., 1933, 761) relative to the occurrence of sub-electrons and electrophotophoresis is shown to be inadequate for the explanation of these phenomena.

A. J. M.

Explanation of transference of charge and electrophotophoresis. K. SITTE (Physikal. Z., 1934, 35, 345—346).—A reply to Lustig and Reiss (preceding abstract). A. J. M.

Nature of electrodic capacity with alternating current. N. THON (Compt. rend., 1934, 198, 1681—1683; cf. this vol., 493). B. W. B.

Influence of gases on the unidirectional conductivity of the silicon-carbon couple. (MILLE.) M. QUINTIN (Compt. rend., 1934, 198, 1677—1679; cf. this vol., 240).—The influence of occluded gases on the characteristic of the Si-(SiO₂)-C rectifier was studied. Asymmetry of characteristic was increased by evacuation or heating, was less in He than in A, and varied with gaseous pressure. The results may be attributed to either ionic or electronic effects. B. W. B.

Electrical conductivity of magnesia at high temperatures. E. ROUSSEAU (Chim. et Ind., 1934, 31, Spec. No., 755—758).—The resistivity, R , of a crystal of MgO follows Joffé's law ($\log r = A + B/T$) between 1400° and 1700°. R for powder MgO does not follow Joffé's law above 1600°. Additions of MgO to Al₂O₃, or vice versa, produce a fall in R and the system has min. at the eutectics. R of spinel is close to that of MgO. Additions of metal oxides, SiO₂, and P₂O₅ improve the conductivity of MgO, the greatest effect being with 10% P₂O₅. T. W. P.

Refraction and dispersion of crystals. X. Connexions between refraction and absorption of halogen ions in crystalline and dissolved state. P. WULF (Z. physikal. Chem., 1934, B, 25, 177—207; cf. this vol., 245).—Dispersion formulæ for the cryst. alkali halides have been derived by a graphical method (A., 1933, 765). With chlorides of the rock-salt type the first characteristic frequency of the dispersion formula runs parallel with the Madelung potential, P . With NaBr and KBr the frequency of the first absorption max. does not run parallel with P , and probably increases with fall in the frequency of the centre of gravity of the group of absorption bands. With chlorides of the rock-salt type the probability of transition corresponding with the first absorption max. does not change by more than 5% with change in the cation. The val. for CsCl is 8/6 times this val. For Cl', Br', and I' in aq. solution the characteristic frequency and probability of transition are considerably reduced compared with the cryst. state. The variation with concn. of the ionic refraction of dissolved electrolytes is not irreconcilable with the position of the absorption max. not varying with concn. R. C.

Molecular refractivity of sodium chloride. F. H. NEWMAN (Phil. Mag., 1934, [vii], 17, 1072—1075).—Factors affecting mol. refraction for an electrolytic solution are discussed. Data for NaCl indicate that ions in solution are more similar to gaseous ions than ions in crystals. Determinations of n for NaCl in the concn. range 0.002—0.0001 equiv. per 1000 g. of H₂O give the val. $[R_L]_D^{20} = 9.05^\circ$, at infinite dilution, and show definite changes at concns. below 0.002 and 0.0005 equiv. per 1000 g. of H₂O. N. M. B.

Anomalous dispersion by diffraction. A. H. PFUND (J. Opt. Soc. Amer., 1934, 24, 121—124).—

Diffraction bands with black min. are produced with a single slit ruled in an absorbent film. These bands are sharpest in the absorption band of the film, and the anomalous dispersion of org. dyes is thus conveniently studied. Films of Au also appear to exhibit anomalous dispersion. A. G.

Rotatory powers of alkaline-earth tartrates. I. PEYCHÈS (Compt. rend., 1934, 198, 1600—1602; cf. this vol., 13).— $[\alpha]$ (at λ 5461) was determined for tartrates of Sr and Ba at concns. up to 0.04M and of Ca up to 0.012M, the more conc. solutions being supersaturated. All showed increase of $[\alpha]$ with concn. (cf. Darmois, A., 1928, 1320). Owing to incomplete dissociation the order of $[\alpha]$ for the Ca, Sr, and Ba salts agrees with that of crystal- instead of hydrated-cationic radii. B. W. B.

Magnetic rotatory dispersion of water in the ultra-violet. G. BRUHAT (J. Phys. Radium, 1934, [vii], 5, 152).—Previous results (cf. this vol., 13) are compared with other available data obtained by photographic methods. N. M. B.

Magnetic rotatory dispersion and refraction of aqueous solutions of cerous sulphate. R. W. ROBERTS, L. A. WALLACE, and I. T. PIERCE (Phil. Mag., 1934, [vii], 17, 934—961; cf. this vol., 13).—Using the polarimetric method at 22.2° for three concns., the sp. rotations of Ce₂(SO₄)₃ and La₂(SO₄)₃ are negative, and, for Ce₂(SO₄)₃, independent of concn. Magnetic rotatory dispersion of Ce₂(SO₄)₃ in the range 5780—3341 Å. calc. by taking into account absorption bands at 2960 and 2540 Å. confirms the ground state of the Ce⁺⁺⁺ ion as $4^2F_{5/2}$ and not $5^2D_{3/2}$. The mol. refraction is independent of the concn. N. M. B.

Magnetic double refraction of solutions of paramagnetic salts. C. MÜNSTER (Z. Physik, 1934, 88, 593—600).—Magnetic double refraction observed at different temp. and concn. with aq. solutions of Ce nitrate shows that this is due to the undissociated mol. A. B. D. C.

Affinity. III. T. DE DONDER (Bull. Acad. roy. Belg., 1934, [v], 20, 268—281; cf. A., 1933, 211, 450, 1232).—Mathematical. N. M. B.

Existence of bi-radicals. E. MÜLLER, W. KLEMM, and W. SCHÜTH (Naturwiss., 1934, 22, 335).—A mol. of the formula $\cdot\text{CPh}_2\text{N}\cdot\text{N}\cdot$ should be paramagnetic at room temp., but is actually diamagnetic. The bi-radical formula is not acceptable. A. J. M.

Structure and properties of homopolar compounds. IV. A. DIBROVA (Ukrain. Chem. J., 1933, 8, 171—178).—Theoretical. R. T.

Configuration of some optically active hexaco-ordinated complexes. J. P. MATHIEU (Compt. rend., 1934, 198, 1598—1600).—Werner's solubility rules (A., 1918, ii, 822) indicate that $l\text{-}[\text{Rh en}_3]^{--}$ and $d\text{-}[\text{Co en}_3]^{--}$ [$\text{en} = \text{C}_2\text{H}_4(\text{NH}_2)_2$] should have similar configurations; also $l\text{-}[\text{Co}(\text{C}_2\text{O}_4)_3]^{--}$ and $d\text{-}[\text{Rh}(\text{C}_2\text{O}_4)_3]^{--}$ (α_D in all cases; thus neglecting the possible effects of anomalous dispersion). Jaeger (A., 1919, ii, 310) ascribes dissimilar configurations on other evidence. The mol. dichroisms, coeffs. of absorption, and $M[\alpha]_D$ vals. of $[\text{Co en}_3]\text{Br}_3 \cdot 2\text{H}_2\text{O}$, $[\text{Rh en}_3]\text{I}_3 \cdot \text{H}_2\text{O}$, $[\text{Ir}(\text{C}_2\text{O}_4)_3]\text{K}_3 \cdot 2\text{H}_2\text{O}$, and $[\text{Rh}(\text{C}_2\text{O}_4)_3]\text{K}_3 \cdot 2\text{H}_2\text{O}$ were

determined over the absorption region, and indicate that, whatever the sign of $M[\alpha]_D$, complex ions of the same series giving salts of the same relative solubilities show a Cotton effect of the same sign. B. W. B.

Paramagnetism and diamagnetism of substances in magnetic fields of low intensity. A. O. RANKINE (Proc. Physical Soc., 1934, 46, 391—407).—A preliminary form of magnetic gradiometer has been found suitable for demonstrating the para- or dia-magnetism of substances of small susceptibility. Small magnetising fields of the order 50 gauss are used. The principle of the instrument may be adapted to the construction of a highly sensitive galvanometer.

N. M. B.

Paramagnetic rotation and susceptibility in manganous and ferric salts. J. H. VAN VLECK and W. G. PENNEY (Phil. Mag., 1934, [vii], 17, 961—987).—Formulæ are deduced for the temp. variation and anisotropy in the susceptibility of Mn^{II} or Fe^{III} compounds of high magnetic dilution, with a discussion of the Faraday effect. Theoretically, if the cryst. field has perfect cubic symmetry, the susceptibility and paramagnetic part of the Verdet const. are probably proportional, and should show the same temp. dependence. Qual. comparison is illustrated with data for spessartite and dialogite.

N. M. B.

Magnetic properties of cerium, lanthanum, and neodymium at different temperatures. F. TROMBE (Compt. rend., 1934, 198, 1591—1593; cf. A., 1933, 475).—The magnetic susceptibilities, χ , at 16° and 5000 gauss of Ce, La, and Nd containing < 0.05% Si and 0.02% Fe were 17.8, 1.2, and 39.5×10^{-6} , respectively. For the ranges 273—109° and 109—90° abs., Nd gave moments of 17.8 and 11.3 Weiss magnetons; the former val. is comparable with that of Gorter and Haas (A., 1932, 448) for $Nd_2(SO_4)_3 \cdot 8H_2O$ and with the theoretical val. for Nd^{III} .

B. W. B.

Magnetic susceptibility of ammonium hexabromo-hypoantimonate. N. ELLIOTT (J. Chem. Physics, 1934, 2, 298—299).—The val. obtained is -0.036×10^{-6} , the substance thus being diamagnetic, and not containing unpolymerised complexes involving Sb^{IV} . The probable structure is $(NH_4)_4Sb^{III}Sb^{IV}Br_{12}$.

N. M. B.

Magnetic susceptibilities of gases and vapours. S. R. RAO and G. SIVARAMAKRISHNAN (Proc. Physical Soc., 1934, 46, 318—323).—An improved retorsion method with bifilar suspension and provision for the systematic elimination of known sources of error is described. The mol. susceptibility of CO_2 was $-(20.79 \pm 0.08) \times 10^{-6}$.

N. M. B.

Magnetic susceptibilities of gases and vapours. G. SIVARAMAKRISHNAN (J. Annamalai Univ., 1934, 3, 48—58).—Using the method described in the preceding abstract, the molar susceptibility of C_6H_6 vapour at 32° was found to be 79.6×10^{-6} .

R. S. B.

Zero-point energy of molecular crystals. V. DEITZ (J. Chem. Physics, 1934, 2, 296).—Vals. and calc. heats of sublimation at 0° abs. are given for He, Ne, A, H_2 , N_2 , CO, NO, O_2 , HCl, HBr, and HI.

N. M. B.

Vibrations of tetrahedral pentatomic molecules. I. Potential energy. II. Kinetic energy

and normal frequencies of vibration. (MISS) J. E. ROSENTHAL (Physical Rev., 1934, [ii], 45, 538—544; cf. A., 1933, 204).—Mathematical. N. M. B.

Vibration frequencies of atoms. B. N. SEN (J. Indian Chem. Soc., 1934, 11, 243—248).—A formula for the calculation of at. frequencies from the parachor, at. vol., valency, N , at. wt., and e gives results in good agreement with experimental and other calc. vals.

N. M. B.

sp^3 Configuration of carbon, and [theory of structure of] CH_4 . J. H. VAN VLECK (J. Chem. Physics, 1934, 2, 297—298).—A previous paper (cf. this vol., 241) is extended with the help of data due to Edlén (cf. A., 1933, 991).

N. M. B.

Mutual repulsive potential of closed shells. W. E. BLEICK and J. E. MAYER (J. Chem. Physics, 1934, 2, 252—259).—Mathematical. By means of a generalised Heitler-London method, a representation, in terms of a small no. of integrals, of the mutual potential of two ions or atoms having a rare gas electron configuration is deduced.

N. M. B.

Ground state of C_2 and O_2 and the theory of valency. W. HEITLER and G. PÖSCHL (Nature, 1934, 133, 833—834).—The apparent contradiction between the experimentally-determined ground states of C_2 and O_2 and the quantum-mechanical theory of the chemical linking is explained.

L. S. T.

Term structure of the non-collinear triatomic molecule of type X_2Y . A. V. BUSHKOVITCH (Physical Rev., 1934, [ii], 45, 545—549).—Mathematical. Group theory methods are employed.

N. M. B.

Lattice energies of RbBr and NaCl. L. HELMHOLTZ and J. E. MAYER (J. Chem. Physics, 1934, 2, 245—251).—The calc. vals., from electrical measurements of the ion emission through an orifice in an equilibrium chamber at high temp. containing salt vapour, are 151.3 and 181.3 ± 3.0 kg.-cal., respectively; the corresponding electron affinities are 84.2 for Br and 88.3 kg.-cal. for Cl.

N. M. B.

Capillary depression of mercury in wide tubes. J. STÜLLA-GÖTZ (Physikal. Z., 1934, 35, 404—407).—By interference experiments it is shown that in tubes of diameter > 45 mm. capillary forces no longer exert an influence on the Hg meniscus.

A. J. M.

Rocking-curves by transmission of the X-ray beam through calcite crystals. T. R. CUYKENDALL and S. W. BARNES (Physical Rev., 1934, [ii], 45, 617—619).—Using a two-crystal spectrometer, rocking-curve widths for calcite crystals in the (1, -1) position are reported at 0.208 Å. ($W K\alpha_1$). The results of etching the faces of two crystals are discussed.

N. M. B.

Nucleus formation in silver halide crystals. M. SAVOSTANOVA and A. TOPORETZ (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 225—231).—The colloidal particle size in AgCl and AgBr coloured by ultra-violet light has been measured ultramicroscopically and by finding the position of max. light absorption. Further illumination of the colloidal particles with light absorbed by them, but not by the AgCl or AgBr crystal, leads to their disappearance. In crystals containing

excess of Ag, growth of the particles occurs on further illumination.

H. J. E.

Rate of nucleation of copper sulphate in a vacuum. N. F. H. BRIGHT and W. E. GARNER (Nature, 1934, 133, 570).—The rate of growth of the centres of dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ varies with the crystal direction. When a crystal is removed, dried, and placed in a high vac., no nuclei appear until after an induction period (I) (approx. 100 min. at 18°), when the no. of nuclei begins to increase linearly. (I) is probably due to the slow rate of growth of the nuclei when first formed.

L. S. T.

Disintegration of sputtered deposits. E. A. JOHNSON and L. HARRIS (Physical Rev., 1934, [ii], 45, 630—634).—The anomalous distribution pattern obtained when an edge or slit is interposed between a cathode and a receiver is due to disintegration of the deposit by neutralised positive ions of the sputtering gas reflected from the cathode, indicating that the sputtered particles either have a low velocity or consist of at. clusters. A similar effect is caused by electrons having an energy > 2000 volts.

N. M. B.

X-Ray investigation of rock-salt. "Ideal" reflecting rock-salt. M. RENNIGER (Naturwiss., 1934, 22, 334—335).—X-Ray examination of a crystal of rock-salt showed it to be ideal. The mosaic character of rock-salt is not inherent, but is caused during growth, or by later changes.

A. J. M.

X-Ray studies in the system nickel-oxygen-water. III. K-Absorption limits of nickel in various oxide hydrates. R. W. CAIRNS and E. OTT (J. Amer. Chem. Soc., 1934, 56, 1094—1096).—The results obtained support the contention (A., 1933, 352) that $\text{Ni}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ contains Ni^{III} .

E. S. H.

Multiple Laue spots from aluminium crystals. A. KOMAR and W. OBUKHOFF (Nature, 1934, 133, 687).—The distribution of intensity along the Laue spots from thick (6 mm.) deformed Al crystals (I) depends on the degree of plastic deformation. Multiple Laue spots previously described may be due to reversible or irreversible changes in the perfection of the crystals, and also to focussing in the case of deformed (I).

L. S. T.

Crystal structure of the compounds LaMg_3 , CeMg_3 , and PrMg_3 . A. ROSSI and A. IANDELLI (Atti R. Accad. Lincei, 1934, [vi], 19, 415—420).—These compounds are cubic, with a 7.48, 7.37, 7.37 Å., d_{calc} . 3.35, 3.43, 3.52 for the La, Ce, and Pr compounds, respectively. At. co-ordinates and a spatial model are given.

O. J. W.

Calcium sulphate hemihydrate. W. A. CASPARI (Nature, 1934, 133, 648).—Crystals (I) of the "hemihydrate" grown in dil. HCl, H_2SO_4 , or HNO_3 belong to the trigonal system, and consist of hexagonal prism form; a 6.76, c 6.24 Å., with three mols. per cell and d only slightly $<$ that of anhydrite (II). "Dead-burning" converts (I) into pseudomorphs consisting of ordinary (II), which appears to be dimorphous with the orthorhombic, comparatively inert modification, and the trigonal form, stable up to approx. 200° . This takes up H_2O zeolitically and the behaviour of this form in contact with H_2O causes plaster to set.

L. S. T.

Colusite, $(\text{Cu,Fe,Mo,Sn})_4(\text{S,As,Te})_{3-4}$. W. H. ZACHARIASEN (Amer. Min., 1933, 18, 534—537).—Colusite is cubic; a 5.304 ± 0.001 Å.

CH. ABS.

X-Ray study of the n -aliphatic alcohols, $\text{C}_{10}\text{H}_{21}\text{OH}$ to $\text{C}_{18}\text{H}_{37}\text{OH}$. D. A. WILSON and E. OTT (J. Chem. Physics, 1934, 2, 231—238).—Spacings along identity periods perpendicular to the 001 planes (c spacings) were measured at room temp. and -50° , and, when plotted against the no. of C atoms in the chain, show the existence of two cryst. modifications, the second appearing only in members having an even no. of C atoms. The ordinary (α) forms crystallise with the c axis approx. at right angles to the 001 plane, and the others (β) have the c axis at approx. $51^\circ 55'$ to the 001 plane, the packings at the ends of the mols. being different for the two cases.

N. M. B.

Intensities of reflexion of a series of n -aliphatic alcohols. D. A. WILSON and E. OTT (J. Chem. Physics, 1934, 2, 239—244; cf. preceding abstract).—Comparison of observed and calc. intensities of c spacings of the α -modification of the series $\text{C}_{13}\text{H}_{27}\text{OH}$ — $\text{C}_{18}\text{H}_{37}\text{OH}$ gives good vals. for the co-ordinates, projected on the c axis, of the constituent atoms.

N. M. B.

Alternation in long-chain compounds. II. X-Ray and thermal investigation of the triglycerides. C. E. CLARKSON and T. MALKIN (J.C.S., 1934, 666—671).—The triglycerides from tridecain to tristearin exist in three solid forms: a stable, high-melting β -form, which separates from solvents or slowly from the molten glyceride maintained only slightly below its m.p.; a lower-melting monotropic metastable α -form which separates from the molten glyceride when cooled more rapidly; and a still lower-melting glass form obtained by rapid cooling of the melted glyceride. The m.p. of the glass and α -forms lie on smooth curves, but those of the β -form show alternations. X-Ray examination shows that in the β -form the long C chains are tilted across the planes formed by the terminal Me groups, whilst in the α -forms they are perpendicular to these planes. The results support Malkin's views on alternation (A., 1932, 326). A structure for the glyceride mol. is suggested.

J. W. S.

X-Ray photographs of crystalline pepsin. J. D. BERNAL and D. CROWFOOT (Nature, 1934, 133, 794—795).—Crystals (I) of pepsin, c/a 2.3 ± 0.1 , are birefringent and positively uniaxial, with a good interference figure, when examined in their mother-liquor. On exposure to air the birefringence rapidly diminishes, and X-ray photographs give only a blackening, indicating complete alteration of the crystal. Photographs of (I) in their mother-liquor give a 67 and c 154 Å., approx. or multiples of these vals., and using the val. d 1.32 the mol. wt. of the unit cell is 478,000. (I) contain approx. 50% of H_2O removable at room temp. Possible mol. structure is discussed.

L. S. T.

X-Ray photographs of crystalline pepsin. W. T. ASTBURY and R. LOMAX (Nature, 1934, 133, 795).—A discussion (cf. preceding abstract).

L. S. T.

Structure of rubber studied by means of electron rays. G. BRUNI and G. NATTA (*Atti R. Accad. Lincei*, 1934, [vi], 19, 206—211).—Electron diffraction measurements give the three fundamental distances a 6.53, b 7.68, c 9.60 Å. for thin films of rubber $0.5\text{--}3.0 \times 10^{-5}$ cm. thick. The unit cell, containing 4 isoprene groups, has V 481.10×10^{-24} c.c. and d_{calc} 0.94. Cryst. rubber is rapidly transformed into the amorphous form by the action of the electron beam, probably due to a thermal effect.

O. J. W.

Röntgenography of liquids. II. X-Ray diffraction of allylthiocarbimide and methylaniline mixtures. I. I. TSCHALENKO (*Ukrain. Chem. J.*, 1933, 8, 140—150).—Diffraction data indicate that $\text{C}_3\text{H}_5\text{SCN}$ (I) undergoes association to double mols. on X-ray irradiation, the distance between the optical centres of the constituent mols. being 8.5 Å. Mixtures of (I) and NHPhMe (II) give diffraction corresponding with formation of a 1:1 compound [magnitude of mol. 9.4 Å., corresponding with 4.25 Å. for (I), and 5.1 Å. for (II)].

R. T.

Present position of the study of the nature of liquid structures by diffraction of X-rays. G. W. STEWART (*Kolloid-Z.*, 1934, 67, 130—135).—A review.

E. S. H.

Accurate electron diffraction measurements. G. I. FINCH and A. G. QUARRELL (*Nature*, 1934, 133, 758).

L. S. T.

Electron diffraction by "crossed lattice powder." A. STEINHEIL (*Z. Physik*, 1934, 89, 50—57).—Diffraction of 60- to 75-kv. electrons by mica powder shows effects due to both crossed and space lattices.

A. B. D. C.

Influence of electron streaming on the dielectric strength of crystals. A. VALTER and L. INGE (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 2, 68—71).—Experiments with coloured rock-salt in which the electron concn. can be altered by illumination indicate that conduction in solid insulators is due to the effect of the electric field in drawing out electrons rather than to ionisation by collision.

H. S. P.

Conditions increasing the phenomenon of magnetic viscosity. A. V. MITKEVITCH (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 1, 531—537).—The magnetic viscosity in soft Fe is much greater when the field in the exciting coil is allowed to decrease relatively slowly (through a parallel resistance) than when its circuit is broken suddenly, giving rise to oscillatory conditions. An Fe wire (0.1 mm. diameter) can show magnetic viscosity 30 min. after a change of magnetic force.

J. W. S.

Theory and measurement of the magnetic properties of iron. D. C. GALL and L. G. A. SIMS (*J. Inst. Electr. Eng.*, 1934, 74, 453—468).—The methods of representing ferromagnetic properties by means of vector diagrams and equiv. electric circuits are criticised.

A. J. M.

Magneto-resistance of bismuth, nickel, iron, cobalt, and Heusler alloy by the longitudinal magnetic field at low and high temperatures. Y. MATUYAMA (*Bull. Inst. Phys. Chem. Res. Japan*,

1934, 13, 283—313).—The change of electric resistance by the field up to 1700 gauss, and for the temp. range -196° to 830° , was measured. Magneto-resistances were calc., and their variation with field and temp. is discussed.

N. M. B.

Changes in resistance of metals in magnetic fields. P. KAPITZA (*Magnetismus*, 1933, 1—9; *Chem. Zentr.*, 1933, ii, 2798).—The increase in resistance of metals in a magnetic field varies quadratically with the field strength (I) in weak fields and linearly with (I) in strong fields. With chemically pure or annealed material linearity commences at lower (I). A theory for normal metals can be based on the assumption of a direct action of the magnetic field on the crystal lattice.

L. S. T.

Connexion between magnetisation and electrical resistance of ferromagnetic substances. W. GERLACH (*Magnetismus*, 1933, 10—24; *Chem. Zentr.*, 1933, ii, 2799).

L. S. T.

Resistance and radiation of tungsten as a function of temperature. W. E. FORSYTHE and E. M. WATSON (*J. Opt. Soc. Amer.*, 1934, 24, 114—118).—The log resistance-log temp. curve has a slope of 1.209 between 293° and 1200° abs. and 1.195 between 1200° and 2800° abs.

R. S.

Explanation of superconductivity. J. FRENKEL (*Nature*, 1934, 133, 730—731).—Theoretical.

L. S. T.

Superconductors in a magnetic field. W. J. DE HAAS [with G. J. SIZOO, J. VOOGD, and H. BREMMER] (*Magnetismus*, 1933, 59—73; *Chem. Zentr.*, 1933, ii, 2798).—A discussion.

A. A. E.

Magnetic properties of superconductors. E. F. BURTON (*Nature*, 1934, 133, 684).—Experiments with Sn are described (cf. this vol., 492).

L. S. T.

Theory of metals. R. PEIERLS (*Z. Physik*, 1934, 88, 786—791).—A reply to Kretschmann (this vol., 347).

A. B. D. C.

Molecular theory of external friction. B. DERJAGUIN (*Z. Physik*, 1934, 88, 661—675).—Neglecting intermol. forces of attraction and replacing repulsive forces by quasi-rigid components, empirical formulæ are obtained. Inclusion of cohesive forces gives a generalisation of Amonton's law. The theory can be applied to internal flow of single crystals.

A. B. D. C.

Madelung constants for some cubic lattices. T. S. WHEELER (*Phil. Mag.*, 1934, [vii], 17, 1058).—A correction of the const. for cuprite previously reported (cf. Sherman, A., 1933, 12) is not sustained.

N. M. B.

Strength properties of salt crystals containing water. V. Time variation of solution after-effects with different solvents. K. WENDENBURG (*Z. Physik*, 1934, 88, 727—740).—Dry and wetted NaCl have strength independent of cross-section. Rupture strength measured for crystals dissolving in H_2O , $\text{H}_2\text{SO}_4 + 25\%$ SO_3 , and NH_3 shows time variation up to 2 hr. after immersion, the various solvents acting differently due to dependence on their adsorbability.

A. B. D. C.

Plasticity of bismuth due to occluded gas. W. F. BERG (Nature, 1934, 133, 831; cf. A., 1926, 666). L. S. T.

Slip-bands and twin-like structures in crystals. C. F. ELAM (Nature, 1934, 133, 723).—Slip-bands occurring in crystals of Cu-Zn alloy (48–50% Zn) are described. L. S. T.

Transformation of yellow mercuric iodide into the red form. J. B. M. COPPOCK (Nature, 1934, 133, 570).—In single crystals of the yellow form cryst. from MeOH, nucleation occurs after about 15 min., usually along the whole length of the crystal edge. The interface then moves rapidly across the crystal parallel to the edges. Smaller rhombohedra of the yellow form, obtained by heating the red variety, change into the red form after approx. 5 hr., the reaction spreading slowly inwards from all four edges with the usual parallel advance of the interface. L. S. T.

Is liquid benzene allotropic? E. COHEN and J. S. BUY (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 198–201; cf. A., 1932, 452).—The kink in the v. p. curve of C_6H_6 suggested by Menzies and Lacoss (cf. A., 1933, 668) does not exist, since the relation between $1/T$ and $\log p$ is not linear between 65° and 100° . Their results afford no evidence for allotropic liquid C_6H_6 . H. S. P.

Is liquid benzene allotropic? E. COHEN and J. S. BUY (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 278–280; cf. preceding abstract).—Vals. obtained by various authors for the sp. heat of C_6H_6 at various temp. show unexplainable divergencies. None of the measurements suggests a break in the sp. heat-temp. curve. J. W. S.

Dispersion of sound. Three energy levels. (a) M. E. ROSE, (b) W. T. RICHARDS (J. Chem. Physics, 1934, 2, 260–262, 263).—(a) Mathematical (cf. Richards, this vol., 135).

(b) A note on the above. N. M. B.

"Transition point" of liquid helium. E. A. GUGGENHEIM (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 294–297; cf. this vol., 136).—Theoretical. A transition point of the type postulated by Halpern is thermodynamically impossible. J. W. S.

F.p. of platinum. F. HOFFMANN and C. TINGWALDT (Physikal. Z., 1934, 35, 434–436).—The f.p. of Pt is $1773.8 \pm 1^\circ$. A. J. M.

Heat capacity curves of the simpler gases. V. Heat capacity of hydrogen at high temperatures. Entropy and total energy. Corrected table of free energy above 2000° . C. O. DAVIS and H. L. JOHNSTON (J. Amer. Chem. Soc., 1934, 56, 1045–1047).—Vals. of the above properties have been calc. for the range 250 – 5000° abs. The influence of anharmonic vibration is about 0.5 g.-cal. per mol. per degree at 5000° abs. The influence of mol. stretching is also relatively large and passes through a max. about 3500° abs. E. S. H.

Specific heats of solid metals at high temperatures. XV. Redetermination of the specific heats of palladium. F. M. JAEGER and W. A. VEENSTRA (Proc. K. Akad. Wetensch. Amsterdam, 1934,

37, 280–283; cf. A., 1932, 220).—The max. previously found in the c_p - t and C_p - t curves for Pd were due to experimental error. The c_p - t curve is almost a straight line, but the slope increases slightly above 1125° . The sp. heat and at. heat are given by $c_p = 0.058378 + 0.120548 \times 10^{-5}t + 0.258 \times 10^{-9}t^2$, and $C_p = 6.2288 + 0.12862 \times 10^{-2}t + 0.27528 \times 10^{-7}t^2$. The val. of $3R$ g.-cal. is exceeded for C_p at -150° and for C_v at -120° . J. W. S.

Specific heats of beryllium, germanium, and hafnium at low temperatures. S. CRISTESCU and F. SIMON (Z. physikal. Chem., 1934, B, 25, 273–282).—Measurements extend from 10° abs. to room temp. With Be between 10° and 14° there is an anomaly which at its max. is of the order of the normal val. of the sp. heat at this temp. Ge exhibits an anomaly similar to those observed with grey Sn, Si, and diamond, but whilst the anomaly begins similarly to a Schottky function it goes over into the NH_4 type towards its upper temp. limit. With Hf there is an anomaly with a sharp peak at 75° which resembles the behaviour of ferromagnetic substances at the Curie point. R. C.

Rotational heat of the molecules H^1H^2 and H_2^3 . K. CLUSIUS and E. BARTHOLOME (Naturwiss., 1934, 22, 297).—The variation of sp. heat between 35° abs. and the temp. of liquid air of mixtures of the H isotopes was determined, and the rotation heat of H^1H^2 and H_2^3 found. H^1H^2 is a normal diat. rotator. No mol. modifications exist. H_2^3 consists at room temp. of two mol. types, and the mixture contains 2 parts of ortho- H_2^3 and 1 part of para- H_2^3 . The equilibrium $2H^1H^2 \rightleftharpoons H_2^3 + H_2^3$ is fixed by cooling from 1000° to room temp. The equilibrium ortho- $H_2^3 \rightleftharpoons$ para- H_2^3 lies towards the left in the absence of catalysts at 14° abs. It is fixed by cooling to 12° abs. A. J. M.

Spectroscopic calculation of molecular heats of air, oxygen, and nitrogen. M. TRAUTZ and H. ADER (Z. Physik, 1934, 89, 1–11).—Rotation and vibrational contributions to the mol. heat capacities of air, N_2 , and O_2 are determined from spectroscopically observed frequencies and moments of inertia. A. B. D. C.

Rotation heat capacity of water vapour. M. TRAUTZ and H. ADER (Z. Physik, 1934, 89, 12–14).—Mecke's analysis of the H_2O spectrum (A., 1933, 6) is used to determine this heat capacity. A. B. D. C.

Calculation of the molecular heat of molecular and atomic chlorine. M. TRAUTZ and H. ADER (Z. Physik, 1934, 89, 15–23).—The heat capacities of Cl and Cl_2 are determined, taking into account isotopic effects. A. B. D. C.

The "chemical constant." K. POSTHUMUS (Rec. trav. chim., 1934, 53, 598–606).—The first part of a calculation of errors due to simplifying assumptions in integrating the Clausius-Clapeyron equation. F. L. U.

Fundamental equation of gases. V. K. JABECZYŃSKI (Rocz. Chem., 1934, 14, 171–176).—In the form of van der Waals' equation (I) given previously (this vol., 481), $f_1(w)$ may be calc. from $f_1(w) = w^2[(dp/dT)_w T - p] = \text{const.}$ (a_1) for a given gas, corre-

sponding with van der Waals' const. a , but independent of temp. and pressure. (I) is given in the form $(p+a_1/w^2)(w-b)=[R+(w-b)f_2(w)/w^2]T$, in which $f_2(w)T/w^2$ represents the repulsive force between gaseous mols. R. T.

Dependence of "vapour pressure" on temperature above the critical point. M. TRAUTZ and H. ADER (Physikal. Z., 1934, 35, 446—449).—The "v.p." of CO₂ above its crit. temp. has been determined. Using the crit. vol. in the determination of the v.p., the v.-p. curve shows no discontinuities. A. J. M.

Surface vapour pressure and the heat of surface vaporisation. J. SAMESHIMA (Proc. Imp. Acad. Tokyo, 1934, 10, 155—158).—The surface latent heat of vaporisation of myristic acid, calc. from the author's measurements of the temp. dependence of the surface v.p., using the Clausius-Clapeyron equation, is 2457 g.-cal. per mol., from which the range of the attractive force of a mol. is deduced to be 34 Å. R. S. B.

Calculating the vapour pressure of pure liquids. V. A. KIREEV (J. Appl. Chem. Russ., 1934, 7, 1—15).—The v.p., p_a , of a liquid A is given by $\log p_a = L_a \log p_b / L_b + C$, where p_b is the v.p. of a second liquid B , and L_a and L_b are the respective latent heats of vaporisation. The results calc. from this equation are better than those calc. from Henglein's or Düring's equation. A nomogram is given from which the v.p. at various temp. of a no. of liquids can be read. R. T.

Determination of the composition of binary and ternary liquid mixtures by means of V. Meyer vapour density determinations. P. DE PAUW (Chem. Weekblad, 1934, 31, 253—254).—The method of calculating the % of a third substance in a mixture with two others from the vapour density of the binary and ternary mixtures is given, and a convenient form of apparatus for the determination is described. H. F. G.

Viscosity formula for binary mixtures, the degrees of association of the constituents being considered. IX. T. ISHIKAWA (Bull. Chem. Soc. Japan, 1934, 9, 155—160).—The data of previous workers are recal. on the author's theory. D. R. D.

Composition of binary mixtures and their viscosities. B. D. MACLEOD (Trans. Faraday Soc., 1934, 30, 482—493).—The formula $\eta = [\gamma_1 m_1 x_1 / x + \gamma_2 m_2 x_2 / x] M_a / M_c$ is proposed for the viscosity η of a mixture of two liquids. x_1 and x_2 represent the free space per c.c. for the pure liquids, x the corresponding quantity for the mixture for which the molar composition is given by m_1 and m_2 . Vals. of M_a / M_c (actual mean mol. wt./calc. mean mol. wt.) given by this equation agree with the law of mass action applied to the formation of an intermol. compound, but the heat of reaction calc. from the temp. dependence of the dissociation const. shows variations which are attributed to the influence of temp. on the free space. R. S. B.

Porter's rule. A. M. RENTE and F. E. SEUFFERT (Ind. Eng. Chem., 1934, 26, 550—551).—Porter's rule

applies to solutions of electrolytes, and the lines of equal η for different concns. of a given electrolyte are usually concurrent. D. R. D.

Viscosity [and density] of mixed salt solutions.

I. Solutions of potassium and zinc sulphates. A. BANCHETTI (Gazzetta, 1934, 64, 229—234).—Data for 0.1 and 0.5 M aq. solutions at 25° are given. The formation of complexes is suggested. D. R. D.

Refractometric investigation of mixed salt solutions, and ionic deformation. G. SPACU and E. POPPER (Z. physikal. Chem., 1934, B, 25, 460—470).—For solutions of single salts the mol. refraction, R , changes approx. linearly with the concn. Deviations of R from additivity in solutions containing two salts and in which compound formation does not occur are ascribed to ionic deformation, the deviations for KCl+NaCl being $>$ for NaNO₃+KNO₃. The deviation curve consists of two intersecting straight lines. Where compounds are formed the deviation curve is entirely different in form and has one or more max. R. C.

Use of ethyl ether as solvent in electric moment studies. K. HIGASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 57—78).—Et₂O is claimed to have a low enough mol. field to be a suitable solvent for electric moment studies. Results for electric moments, except where stated at 20°, in 10⁻¹⁸ e.s.u.: C₆H₆ (25°) approx. 0, PhMe (25°) 0.3, PhCl (25°) 1.3, COMe₂ 2.2, PhNO₂ (25°) 3.2, EtOH 1.8, BuⁿOH 1.8, amyl alcohol 1.8, borneol 1.7, α -C₁₀H₇OH 1.9, H₂O 1.9, I 0.7, [·CH₂Cl]₂ 1.5, cetyl alcohol 1.81. The polarisation curve of EtOH in Et₂O is approx. linear, in contrast to results with non-polar solvents. The temp. dependence of the electric moments of EtOH, [·CH₂·OH]₂, and AcOH is given and discussed. R. S. B.

Faraday effect of strong electrolytes in aqueous solutions. I. A. OKAZAKI (Mem. Ryojun Coll. Eng., 1933, 6, 181—219).—The magneto-optical rotations of twenty strong electrolytes have been measured, using wave-lengths near to 350 m μ , also their magneto-optical dispersions between 590 and 340 m μ . The sp. rotation is generally nearly independent of concn., but decreases with increasing concn. for HCl and LiCl. The latter effect can be explained by the existence in conc. solutions of undissociated mols. F. L. U.

Heats of fusion of titanium tetrachloride, carbon tetrachloride, and antimony pentachloride. N. NASU (Bull. Chem. Soc. Japan, 1934, 9, 198—205).—The heats of fusion of TiCl₄ (12.90 g.-cal. per g.), CCl₄ (4.40 g.-cal. per g.), and SbCl₅ (6.40 g.-cal. per g.) are calc. from the f.-p. data for binary mixtures. D. R. D.

Composition of the vapour phase over binary mixtures. I. KRITSCHEVSKI and J. KASARNOVSKI (Z. anorg. Chem., 1934, 218, 49—59).—The numerical integration of the Gibbs-Duhem equation has been carried out and applied to the systems CS₂-COMe₂, PhMe-AcOH, and AcOH-H₂O. The accuracy of the calc. val. is limited only by that of the observed relation between total v.p. and composition. F. L. U.

Liquid-vapour equilibria of mixtures of aromatic and non-aromatic hydrocarbons. III. Mixtures of benzene and non-aromatic hydrocarbons. M. MIZUTA (J. Soc. Chem. Ind. Japan, 1934, 37, 113B).—The shape of the equilibrium curve for mixtures of C_6H_6 with light petroleum b.p. 50–97° shows that C_6H_6 could be easily concn. in the vapour phase up to 0.7 mol. fraction, but that further concn. would be difficult. A. G.

Vapour-liquid equilibrium of hydrocarbon mixtures. H. A. BEATTY and G. CALINGAERT (Ind. Eng. Chem., 1934, 26, 504–508).—Data are recorded for the following systems at the temp. given: C_6H_6 -cyclohexane (78.8°); Δ^7 -heptene- n - C_7H_{16} (I) (97.2°); (I)- $\beta\beta\delta$ -trimethylpentane (II) (97.2°); (I)-methyl-cyclohexane (97.2°); (II)- n - C_8H_{18} (III) (98.1°); (I)-(III) (97.2°); C_6H_6 -PhMe (79.6°); n - C_8H_{18} -(I) (67.5°). The effects of small deviations from the ideal mixture law on the no. of plates required in fractionation are tabulated. D. R. D.

Determination of azeotropic composition. Azeotropes of benzene and cyclohexane. A. BOUZAT and M. SCHMITT (Compt. rend., 1934, 198, 1923–1925).—The compositions of azeotropic mixtures (I) of C_6H_6 and cyclohexane have been determined for a range of pressure. The % of C_6H_6 in (I) diminishes with increasing pressure (cf. Merriman J.C.S., 1913, 103, 1807). B. W. B.

B.p. of concentrated solutions of the system $(K, NH_4)(NO_3, Cl)$. S. I. ARONOVA and Z. N. LUNSKAYA (Trans. Sci. Inst. Fertilisers, Moscow, 1932, No. 92, 139–148). CH. ABS.

Concentration by partial condensation in two-component systems. E. KIRSCHBAUM (Chem. Fabr., 1934, 7, 109–111).—The enrichment of the more volatile substance by partial reflux condensation is discussed, and a method is given for deriving the "enrichment curves." A typical example is given for the system C_6H_6 -PhMe. The assumption that the falling liquid is in equilibrium with the adjacent vapour leads to a mean divergence of –60% from experimental results, whilst if it is assumed that the condensed and uncondensed vapours are in equilibrium the mean error is +27%. The author's treatment involves a mean error of only +1.9%. H. F. G.

Diffusion in metals. W. SEITH, E. HOFER, and H. ETZOLD (Z. Elektrochem., 1934, 40, 322–326; cf. A., 1932, 1195).—Velocities of diffusion of Mg, Cd, Ni, and Hg in Pb, and of Pb and Hg in Cd have been measured. Diffusion of Pb in Sn has been observed; diffusibility in Pb decreases in the order Au, Ag, Mg, Cd, Hg, Bi, Tl, Sn. F. L. U.

Superconductivity of alloys. G. TAMMANN (Z. Metallk., 1934, 26, 61).—From a consideration of recent work of Meissner and of Allen rules are derived for the onset of superconductivity in solid solutions, eutectics, and two-phase alloys and the effect thereon of magnetic fields. A. R. P.

Theory of transition of metallic mixed phases. G. BORELIUS (Ann. Physik, 1934, [v], 20, 57–74).—An expression for the free energy of mixed phases as a function of the extent of disorder of atoms is derived

and tested by reference to the X-ray structure of the alloys and resistance data. A. J. M.

Eutectic of the system antimony-lead. O. QUADRAT and J. JIKŮSTĚ (Chim. et Ind., 1934, 31, Spec. No., 485–489).—Melts containing 20, 15, and 13% Sb deposit crystals of Sb, leaving a eutectic containing 11.4–11.5% Sb, and not the previously recorded 13% Sb. R. S.

Electrochemical and X-ray examination of solid thallium-lead alloys. A. ÖLANDER (Z. physikal. Chem., 1934, 168, 274–282).—The potential of $Tl_{solid}|(Na, K, Tl)OAc|(Tl, Pb)_{solid}$ and its temp. coeff. have been measured for forty-one alloy electrodes at 245–295°, and X-ray diagrams of various Tl-Pb alloys obtained. The lattice consts. show that the boundary between α and β phases is at 54.6 at.-% Tl. Between 54.6 and 92.5 at.-% Tl there is an intermediate phase, Tl_7Pb , which accounts for Kurnakow's conductivity data (A., 1909, ii, 855). R. C.

Electrical conductivity and equilibrium diagram of binary alloys. XII. System lithium-bismuth. G. GRUBE, H. VOSSKÜHLER, and H. SCHLECHT (Z. Elektrochem., 1934, 40, 270–274).—The system forms the compounds Li_3Bi (m.p. 1145° without decomp.) and $LiBi$ (formed by a peritectic reaction at 415°). $LiBi$ exists in two polymorphic forms, with a transition temp. at 400°. The formation of solid solutions has not been observed. E. S. H.

Microscopical examination of iron-tin reaction products. W. D. JONES and W. E. HOARE (Iron and Steel Inst., May, 1934, Advance copy, 8 pp.).—Annealing and quenching experiments and diffusion tests at various temp. have afforded evidence of the existence of the compounds $FeSn_2$, $FeSn$, and Fe_2Sn . $FeSn$ decomposes into Fe_2Sn and Sn at 710–850°. No evidence for the existence of a γ -phase at 68.5% Sn and 850° could be obtained (cf. Ehret and Westgren, A., 1933, 562). A. R. P.

Nickel-chromium system. E. R. JETTE, V. H. NORDSTROM, B. QUENEAU, and F. FOOTE (Amer. Inst. Min. Met. Eng., Inst. Met. Div., Tech. Pub., 1934, No. 522, 11 pp.).—X-Ray investigations show that at < 1150° there are two terminal solid solutions with an intervening two-phase area. On the Cr side the solubility of Ni in Cr is low, but increases rapidly at > 900°. The solubility of Cr in Ni increases uniformly and rapidly with rise in temp., that at 1153° being nearly 53 wt.-% Cr, which is beyond the eutectic point as determined by thermal analysis. The only structures observed were body-centred Cr, face-centred Ni, and occasionally rhombohedral Cr_2O_3 . CH. ABS.

Alloys of platinum with chromium. V. A. NEMLOV (Z. anorg. Chem., 1934, 218, 33–44).—The Brinell hardness-composition curve of Cr-Pt alloys shows well-marked min. corresponding with compounds Cr_2Pt and CrPt. Examination of the microstructure confirms the existence of the latter. Alloys quenched from a high temp. show only mixed crystals, from which CrPt separates on annealing. In annealed specimens there is a continuous series of mixed crystals between 0 and 25 at.-%, and another between 65 and 100 at.-% Pt. The electrical resistance rises very

steeply with increasing Cr content up to 13 at.-% Cr, beyond which the alloys are no longer ductile. Alloys containing 4–5% Cr have about five times the resistance of Pt, and a higher m.p. H_2SO_4 , HCl, and HNO_3 , dil. or conc., show no action either at room temp. or at their b.p. on polished surfaces of alloys with a Cr content ≥ 14 at.-%. F. L. U.

Transition of β -brass. H. VON STEINWEHR and A. SCHULZE (Physikal. Z., 1934, 35, 385–397).—The thermal change and the variation of the expansion, thermo-electric force, and resistance with temp. show that the transition is not sudden, but takes place over a temp. range (430–480°). The heat change is 3 g.-cal. per g. Equilibrium is rapidly attained at any given temp. A. J. M.

Distribution of thorium-B in some metals. W. SEITH and A. KEIL (Z. Metallk., 1934, 36, 68–69).—The metal obtained by electrolysis of a molten mixture of KCl and $PbCl_2$ or $TlCl$ containing Th-B (I) gives a radiogram showing regular distribution of (I) throughout. When Cd or Bi is prepared similarly from a bath containing traces of Pb and (I), both these are irregularly distributed along the crystal boundaries, and on annealing tend to migrate towards the outside of the ingot. Th-C distributes itself homogeneously throughout Bi, and by its aid self-diffusion of Bi can be studied. A. R. P.

Equilibrium diagram for ternary alloys. V. FISCHER (Z. Metallk., 1934, 26, 80–82).—The use of an orthogonal plane co-ordinate system for representing the equilibrium of ternary alloys is illustrated by reference to the Ni-Cu-Mn, Cu-Ag-Au, and Ag-Pb-Sn systems. A. R. P.

Constitution and properties of the alloys of magnesium with aluminium and copper. A. PORTEVIN and P. BASTIEN (Chim. et Ind., 1934, 31, Spec. No., 490–518).—Thermal analysis of alloys rich in Mg indicates a liquidus from which the separating solid phases are Mg , Mg_4Al_3 , Mg_2Cu , and $Mg_2Cu_3Al_2$; the eutectics Mg 56.5, Al 26.5, Cu 17%, m.p. 412°, and Mg 67.5, Al 0.5, Cu 32%, m.p. 484°, two saturated solid solutions (a) rich in Mg: Mg 85, Al 8.8, Cu 6.2%, (b) rich in Mg_4Al_3 : Mg 58, Al 41.4, Cu 0.6%. Micrographic data, hardness, coeff. of expansion, density, and electrical conductivity data are also recorded. Alloys containing 12% Cu can be forged, and possess good mechanical properties, hardness, and thermal conductivity, whilst others (Al+Cu $\leq 15\%$) have mechanical properties comparable with those of electron and duralumin. Corrosion of the ternary alloys increases slowly in 1% HCl and more rapidly in 0.5N- $MgCl_2$ with increasing Cu and const. Al content. Corrosion of Mg-Cu alloys in sea- H_2O is reduced by addition of Al, and becomes const. with Al $> 3\%$. R. S.

Properties of ferromagnetic alloys of the ternary system iron-nickel-vanadium. H. KÜHLEWEN [with R. STÖRMER] (Z. anorg. Chem., 1934, 218, 65–88; cf. A., 1930, 1245).—The structure diagram of alloys with up to 30% V shows (1) a region of mixed crystals of space-centred cubic type (α), (2) mixed crystals of face-centred cubic type (γ), and (3) a heterogeneous field of $\alpha+\gamma$ mixed crystals. In

the γ -range the Curie point is depressed by addition of V by about 40° per 1%. Diagrams showing the variation of sp. resistance and various magnetic properties with composition are given. F. L. U.

F.p., m.p., and solid solubility limits of alloys of silver and copper with elements of the B sub-groups. W. HUME-ROTHERY, G. W. MABBOTT, and K. M. C. EVANS (Phil. Trans., 1934, 233, A, 1–97).—Solubility limits have been completely determined in the systems Cu-Ga, Cu-Ge, Cu-Sb, Ag-Al, Ag-Ga, Ag-Cd, and Ag-In. Confirmatory investigations have been made on Cu-Zn, Cu-Al, Cu-As, Ag-Sn, Cu-Zn-Ga, Cu-Zn-Ge, and Cu-Ga-Ge. Formation of solid solutions of the substitutional type is determined primarily by the respective at. diameters of solvent and solute. The at. compositions of alloys of a given f.p. vary inversely as the valency (n) of the solute as far as group V, and those of alloys of a given m.p. are $\propto 1/n^2$ as far as group IV, when solvent and solute are in the same period. Methods are given for the accurate calculation of liquidus points in ternary and quaternary alloys where the binary curves are known. In certain ternary alloys solubility limits can be approx. calc. when the at. size factors are favourable, since the max. solubility of the α solid solution and the part of the solubility curve in which solubility diminishes with fall of temp. are determined mainly by the electron concn. F. L. U.

Apparent mixed crystals. I. A. BENRATH and H. SCHACKMANN (Z. anorg. Chem., 1934, 218, 139–145).—The systems $BaSO_4$ - $KMnO_4$ - H_2O and $CaCO_3$ - $NaNO_3$ - H_2O fulfil the requirements laid down by Grimm for the formation of mixed crystals. No mixed crystals are formed, however, owing to the large differences in solubility between the components. M. S. B.

Ferrites. Formation of solid solution between some ferrites. N. KAWAI (J. Soc. Chem. Ind. Japan, 1934, 34, 174B).—Mixtures containing various proportions of two or three of the ferrites FeO , Fe_2O_3 , NiO , Fe_2O_3 , CuO , Fe_2O_3 , CoO , Fe_2O_3 , ZnO , Fe_2O_3 , CdO , Fe_2O_3 , and MgO , Fe_2O_3 , after heating to sintering, have been examined microscopically and magnetically. It is inferred that solid solutions are formed. R. S. B.

Influence of degree of dispersion on physico-chemical constants. III. E. COHEN and W. A. T. COHEN-DE MEESTER (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 270–274; cf. A., 1933, 19).—The solubility of salicylic acid in H_2O is increased by grinding with Au balls either in the dry state or in contact with H_2O . The results cannot be explained as a cold-working effect. J. W. S.

Solubility of silver chloride. P. C. DAVE and K. R. KRISHNASWAMI (J. Indian Inst. Sci., 16, A, 153–165).—The solubility (S) of AgCl in H_2O and aq. solutions of HNO_3 , $NaNO_3$, KNO_3 , and NH_4NO_3 has been determined nephelometrically between 0° and 50°. S in H_2O at 25° is 1.388×10^{-5} mol. per litre, as compared with 1.373×10^{-5} from conductivity measurements. S in aq. HNO_3 is slightly greater than in H_2O , and independent of concn. In aq. $NaNO_3$ S increases rapidly with concn., reaching

18.4×10^{-5} in a saturated solution, this behaviour being attributed to formation of complex ions.

F. L. U.

Solubility of calcium iodate in aqueous solutions of various electrolytes. J. B. CHLOUPEK, V. Z. DANEŠ, and B. A. DANEŠOVA (Chem. Listy, 1934, 28, 93—94).—Data are recorded for solutions containing 0.002, 0.1, and 0.5*M*-KNO₃, -K₂SO₄, -MgCl₂, and -MgSO₄.

R. T.

Solubilities of calcium hydroxide, calcium iodate, and ammonium perchlorate in dilute ammoniacal solutions. I. M. KOLTHOFF and V. A. STENGER (J. Physical Chem., 1934, 38, 639—643; cf. A., 1932, 1084).—Solubilities have been determined at 25° in aq. NH₃ up to 2*N*. The solubility of CaO is (0.1194—0.016*C*_{NH₃}) g. per 100 c.c. solution. Under the above conditions no complex compounds are formed between Ca(OH)₂ or Ca⁺⁺ and NH₃.

F. L. U.

Amphoteric character of silver hydroxide. E. LAUE (J. Amer. Chem. Soc., 1934, 56, 1249—1250).—A criticism (cf. A., 1933, 773).

E. S. H.

Solubility of silver oxide in water and in alkali. H. L. JOHNSTON, F. CUTA, and A. B. GARRETT (J. Amer. Chem. Soc., 1934, 56, 1250).—A reply (cf. preceding abstract)

E. S. H.

"Induced" solubility of ferric hydroxide and other hydroxides in alkali hydroxide in presence of chromic hydroxide. H. KNOCHE (Kolloid-Z., 1934, 67, 195—203).—Freshly-pptd. Cr(OH)₃ dissolves in aq. NaOH or KOH when < 1 equiv. of alkali is present, forming sols which may solidify to jellies at certain concns. The effect of KOH is > that of NaOH, but the amount required for dissolution of a given amount of Cr(OH)₃ depends on the concn., the velocity of mixing, and on the age of the Cr(OH)₃. The ageing of Cr(OH)₃ is more rapid as the concn. of alkali increases, and is accelerated by NaCl and KCl. The pptd. Cr(OH)₃ from a green CrCl₃ solution ages more quickly than that from a violet solution. Conductometric titration shows that only a small amount of chromite is formed in the alkaline solution.

E. S. H.

Partition of saturated fatty acids between water and toluene. N. DE KOLOSOVSKI and (MLLE.) E. PONOMAREVA (Bull. Soc. chim., 1934, [v], 1, 66—69; cf. A., 1932, 1198).—Data are recorded for butyric and isovaleric acids. The log. partition coeff.—concn. curves for all fatty acids so far investigated are parallel and tend to ∞ at zero concn. They are of the form to be expected in view of the existence of simple mols. in the PhMe and of dissociated mols. in the H₂O.

J. W. S.

Application of distribution methods to the determination of the activity coefficients of molecules in salt solutions. E. LARSSON (Svensk Kem. Tidskr., 1934, 46, 78—83).—These methods often fail owing to mutual solubility of the phases and hydration or association of the solute. Data are given for activity coeffs. of BzOH, salicylic acid, and CH₂Ph·CO₂H in salt solutions, determined by partition with Et₂O, isoamyl ether, and C₆H₆.

Vals. from solubility determinations are given for comparison.

R. P. B.

Fractional precipitation of radiferous barium sulphate. (MME.) B. E. MARQUES (Compt. rend., 1934, 198, 1765—1767).—The distribution of Ra between BaCl₂ solution and BaSO₄ pptd. by 0.01*N*- or 0.001*N*-H₂SO₄ has been studied. Doerner and Hoskins' law (A., 1925, ii, 381) is verified; the distribution coeffs., however, vary slightly with the rate of pptn.

B. W. B.

Theoretical study of the absorption of a very soluble gas by a liquid drop. S. HATTA and A. BABA (J. Soc. Chem. Ind. Japan, 1934, 37, 162—163B).—An equation is derived for the rate of absorption of a gas by a falling drop of liquid. It is assumed that for a very sol. gas the resistance of the liquid film may be neglected, and that the const. is proportional to the *n*th power of the rate of fall.

A. G.

Absorption of ammonia by a water drop. S. HATTA, T. UEDA, and A. BABA (J. Soc. Chem. Ind. Japan, 1934, 37, 164—165B).—The absorption of NH₃ mixed with O₂ by falling drops of H₂O is expressed by the equation previously derived (cf. preceding abstract), when the concn. of the NH₃ and the height of fall are varied.

A. G.

Adsorption of hydrogen by palladium-black under high pressure. V. IPATIEFF, jun., and W. G. TRONOV (J. Physical Chem., 1934, 38, 623—633).—Adsorption isotherms of H₂ in Pd-black have been determined between 1 and 27 atm. at 15°, 25°, 100°, 150°, 200°, and 300°. The isotherms tend to become straightened out at higher temp. There is no indication of saturation at the highest pressure reached.

F. L. U.

Influence of mercury on the electrolytic adsorption of hydrogen by iron. H. PLOUM (Z. Elektrochem., 1934, 40, 267—270).—Small amounts of HgCl₂ in acid or alkaline solutions catalyse the adsorption of H₂ by Fe cathodes. It is probable that a volatile Hg hydride is formed.

E. S. H.

Diffusion of hydrogen through metals: fractionating the hydrogen isotopes. C. G. FINK, H. C. UREY, and D. B. LAKE (J. Chem. Physics, 1934, 2, 301).—A note on a previous paper (cf. this vol., 360).

N. M. B.

Sorption of water vapour on chabasite at various temperatures. A. TISELIUS and S. BROHULT (Z. physikal. Chem., 1934, 168, 248—256).—Sorption isotherms at 50—150° for H₂O vapour pressures of 0.008—15 mm. have been obtained. At the lower temp. these approximate in form to Langmuir's isotherm. The sorption is reversible. The heat of sorption, calc. from the isotherms, is a max. when the amount of H₂O sorbed is about 20%.

R. C.

Vapour-binding power of active charcoal. II. Dependence of the amount of retained gas on the streaming velocity of the replacing gas. III. Dependence on particle size. F. KROZIL and H. WEJROCH (Kolloid-Z., 1934, 67, 161—163, 163—167; cf. this vol., 358).—II. The amount of adsorbed C₆H₆ retained by C after a given time in

an air stream is the greater the less is the velocity of the air, but the amount retained after passage of a given quantity of air is independent of its velocity.

III. When the particle size is < 1.5 mm. the rate of removal of adsorbed C_6H_6 by an air stream is independent of particle size, but with larger particles the initial rate is less, becoming $>$ that for small particles at a later stage. E. S. H.

Sorption of water vapour by cellulose acetate. R. SHINODA (J. Cellulose Inst. Tokyo, 1934, 10, 114—126).—Secondary cellulose acetate (I) adsorbs about twice as much H_2O as primary (I), there being a linear relation between Ac content and adsorption. Kinetically adsorption occurs in two stages, a fast stage for which $\log \{S_\infty / (S_\infty - S_t)\} = Kt$ followed by the slower stage $S = K' + a \log t$, where S is H_2O adsorbed and a is a const. Adsorption falls with rising temp. at const. R.H.; it is less for the following substances than for (I) and falls in the order given: mannan acetate, ethylcellulose, benzylcellulose. A. G.

Adsorption properties of various soluble compounds. J. RAE (Pharm. J., 1934, 132, 607).—Samples of Bi, Ca, and Mg carbonates differ considerably in their methylene-blue absorptions, but these are not related to the apparent d . A. G.

Behaviour of the diamino-acids from protein hydrolysis towards permutit. V. S. SADIKOV and E. V. LINDKVIST-RISAKOVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 575—578).—From the products of hydrolysis of casein, permutit removes up to 93% of the total diamino-acids, and about half the total monoamino-acids. The former cannot be washed out with H_2O , but are almost completely removed with 30% H_2SO_4 . The behaviour of the permutit depends on its origin and composition. J. W. S.

Adsorbing power of some iron hydrates. E. ALLESI (Gazzetta, 1934, 64, 161—168).—The adsorption of Na arsenite from aq. solution by various Fe^{II} and $Fe^{II}-Fe^{III}$ hydroxides is related to the magnetic properties of these hydroxides. The min. adsorbing power corresponds with max. magnetic susceptibility of the hydroxide. The adsorbing power of $Fe(OH)_3$ varies with its method of prep.; e.g., the hydroxide obtained from the cryst. sulphate adsorbs much $<$ that obtained from a solution of a Fe^{II} salt oxidised with hot HNO_3 . O. J. W.

Adsorption of electrolytes at heteropolar crystal surfaces. D. BALAREV and A. KOLUSCHEVA (Kolloid-Z., 1934, 67, 203—207).—Balarev's theory of inner adsorption is discussed. E. S. H.

Determination of surface area by adsorption of water molecules. J. H. DE BOER and C. J. DIPPEL (Z. physikal. Chem., 1934, B, 25, 399—410).— H_2O vapour is very tenaciously adsorbed by powdered CaF_2 or vac.-sublimed films of CaF_2 , and even on exposure to high vac. at room temp. a unimol. adsorbed film still remains. The no. of adsorbed mols. can be ascertained by interaction with Cs and determination of the amount of H_2 or Cs_2O formed. In the complete unimol. film each F' ion of the surface holds one H_2O mol. On heating, the H_2O reacts with the adsorbing F' ions, forming HF and rendering the

surface alkaline. The sp. surface of vac.-sublimed CaF_2 is about 240 sq. m. per g., and the mean thickness of the lamellæ 0.25×10^{-8} to 0.3×10^{-8} cm. In the adsorption of H atoms by a vac.-sublimed film of CaF_2 each F' ion holds one H atom, whereas in the adsorption of I one mol. is adsorbed by every two F' ions. With *o*- and *p*-nitrophenol there are 2 and 4 F' ions, respectively, to each adsorbed mol. in the first layer of adsorbed mols., but a second layer is formed on this by van der Waals forces. R. C.

Nature of adsorption forces. J. H. DE BOER and J. F. H. CUSTERS (Z. physikal. Chem., 1934, B, 25, 225—237).—Polanyi and London's formulæ for van der Waals adsorption give vals. for adsorption energy on C $<$ the observed vals. If the structure and mol. roughness of the surface are taken into account the discrepancy disappears. The rule that energy of adsorption is approx. half the geometric mean of the heats of vaporisation of the two components is accounted for. Mols. with peripherally situated dipoles adsorbed on surfaces constituted of ions will principally be oriented and bound electrostatically. Thus PhOH on NaCl will have the OH group adsorbed electrostatically on the Cl ions, whilst the Ph ring will be held principally by van der Waals adsorption with the flat side parallel to the surface. In van der Waals adsorption the energy is greatest in the fissures or cavities of a surface and the mols. are fixed by preference above the centres of the unit cells. In electrostatic adsorption the energy is greatest on projecting points and edges, and the adsorbed mols. are situated above the ions of the adsorbent. R. C.

Adsorption and amount of adsorbent. III. A. RABINERSON, T. PAKKOVA-KVITZEL, and A. PITTEL (Kolloid-Z., 1934, 67, 154—161; cf. this vol., 359).—In the adsorption of AcOH by C the expression $x = km^{1/n}$ is valid for medium amounts of adsorbent (m). The val. of $1/n$ is not const., but tends towards 1 when m is small and towards 0 when m is great. Anomalies are noted in the adsorption of Me-violet by C. E. S. H.

Mathematical and experimental studies on repeated extraction of adsorption systems in equilibrium. II. J. VOICU (Kolloid-Z., 1934, 67, 148—154; cf. this vol., 485).—Theoretical. E. S. H.

Formation and properties of precipitates. Theory of co-precipitation. II. I. M. KOLTHOFF (Chem. Weekblad, 1934, 31, 230—237, 244—251).—Adsorption on ppts. may involve simple ionic exchange, as in the case of a dye on $PbSO_4$, when the difference between the concns. of the lattice cations and anions increases with the quantity and degree of fineness of the ppt.; true adsorption, at active centres only; true adsorption followed by secondary pptn. of the displaced lattice ions; exchange with a third kind of ion already adsorbed on the surface of the ppt., which is of importance in the washing of ppts.; mol. adsorption; and activated adsorption, in which the adsorbed substance is ionised in the surface layer. Wool-violet (I) forms a unimol. layer on $PbSO_4$ (II), there being 1 mol. of (I) per mol. of (II) in the surface, but with an excess of $SO_4^{''}$ in the solution the saturation point is reached at higher (I) concns., since (I) displaces

SO₄" in the surface layer. Adsorbed dyes retard the rate of crystallisation of (II). Paneth and Vorwerk's view that Pb(NO₃)₂ (III) at low concns. forms unimol. layers on (II) is incorrect; neither (III) nor Na₂SO₄ is adsorbed by (II), even when freshly pptd.

H. F. G.

Applications of a method of capillary analysis. R. DUBRISAY (Chim. et Ind., 1934, 31, Spec. No., 200—202).—The drop method has been used to study the relative effects of lauric, myristic, palmitic, and stearic acid dissolved in C₆H₆ on the C₆H₆-aq. NaOH interfacial tension. Applications of the method to the study of neutralisation processes (*e.g.*, of wines, and the attack of glass by H₂O), and the examination of fatty acids are discussed.

H. J. E.

Simple method of testing the orientation of molecules on the surface of water or aqueous solutions. B. TAMAMUSHI (Bull. Chem. Soc. Japan, 1934, 9, 161—165).—The end-point in Frumkin's method (A., 1925, ii, 856) is found by the abrupt increase in the time of evaporation of the solvent when the surface is saturated. The no. of mols. per sq. cm. of lauric and palmitic acids, cetyl alcohol, and cetyl and myristyl palmitates is scarcely affected by the presence of small amounts of halides or of sucrose.

D. R. D.

Physical and chemical behaviour of molecules on outside surfaces. R. SUHRMANN (Chem.-Ztg., 1934, 58, 411—413).—Unimol. films on solid or liquid surfaces behave like two-dimensional gases. Electrical polarisation of mols. in films is shown by changes in light absorption, in emission potential, and in contact potential.

A. G.

Physical chemistry of the non-wettability of peat by water. M. V. TSCHAPEK and N. E. SAKUN (J. Appl. Chem. Russ., 1934, 7, 197—204).—Adsorption of H₂O from EtOH-H₂O and C₆H₆-H₂O by peat (I) indicates that (I) is a highly hydrophilic substance, with a well-developed surface. Under ordinary conditions it is not, however, wetted by H₂O; this is due to a film of air adsorbed on the surface of (I).

R. T.

Dependence of the action of filter and sorption vessels on the direction of streaming. H. REMY [with K. HOLTHUSEN] (Kolloid-Z., 1924, 67, 167—171).—The sorptive effect of a combination of a loosely-packed wad and a CaCl₂ tube on NH₄Cl fumes depends on whether the fumes pass through the wad or CaCl₂ first; with a tightly-packed wad the effect is independent of the direction. The sorption of SO₃ fumes by combinations of a wad with conc. H₂SO₄ or P₂O₅ is independent of the direction of streaming.

E. S. H.

Origin of osmotic pressure and its theoretical calculation. K. WOHL (Z. Physik, 1934, 88, 800—805, 820—822).—A criticism of Fredenhagen (this vol., 252).

A. B. D. C.

Origin of osmotic pressure and its theoretical calculation. K. FREDENHAGEN (Z. Physik, 1934, 88, 806—819).—A reply.

A. B. D. C.

Supposed kinetic explanation of osmotic pressure. W. HÜCKEL (Z. physikal. Chem., 1934, 168, 308—309).—Polemical.

R. C.

Supposed kinetic interpretation of osmotic pressure. A. EUCKEN (Z. physikal. Chem., 1934, 168, 309—312).—A reply to Hückel (preceding abstract) and defence of the theory that the flow of solvent through a semipermeable membrane is due to the transference of momentum from solute mols. rebounding from the membrane to solvent mols.

R. C.

Influence of dipole fields between solute molecules. I. Osmotic properties. II. Molecular polarisation. R. M. FROSS (J. Amer. Chem. Soc., 1934, 56, 1027—1030, 1031—1033).—I. Theoretical. The osmotic properties of a dil. solution of dipole mols. are derived.

II. Theoretical. The dielectric properties of the same system are derived.

E. S. H.

F.p. of some benzene solutions. C. R. BURY and H. O. JENKINS (J.C.S., 1934, 688—696).—The f.p. depression of C₆H₆ for nineteen substances has been measured by an equilibrium method. Errors in previous f.p. data due to adsorption appear to be small. The results do not support Hildebrand's hypothesis (A., 1921, ii, 307) connecting internal pressure with deviation from ideal behaviour, nor is there evidence of a direct relation between degree of association and dipole moment.

R. S.

Theory of cryoscopic determinations made by mixing the solution with the solid solvent. A. BANCHETTI (Gazzetta, 1934, 64, 221—228).—Expressions are derived for the final temp. and quantity of solid melted when excess of the frozen solvent is added to a solution. Application to Hovorka and Rodebush's experimental results (A., 1925, ii, 772) shows that the quantity of solid melted under the conditions specified by these investigators is negligible for solutions > 0.005*M*, but if it is ignored when the concn. is 0.01*M*, an error of 1—2% in the depression is introduced.

D. R. D.

Theoretical formulæ for the Landsberger method. A. MAZZUCHELLI (Gazzetta, 1934, 64, 213—217).—The fraction of the vapour which would condense in the hot liquid is calc., assuming each bubble to reach equilibrium as it passes through the liquid, and is shown to be very small, indicating that the composition and temp. will not change appreciably during an experiment of normal duration when the solution has reached its b.p. This is confirmed experimentally in the case of resorcinol in Et₂O.

D. R. D.

Cryoscopic determination of total hydration of ions of potassium bromide. F. BOURION and (Mlle.) O. HUN (Compt. rend., 1934, 198, 1921—1923; cf. this vol., 596).—Hydration corresponds with KBr, 8.1H₂O and KBr, 9.6H₂O in 1.0*M* and 0.5*M* solutions, respectively.

B. W. B.

Application of the method of eutectic point lowering. H. MULLER (Compt. rend., 1934, 198, 1774—1776; cf. A., 1933, 906).—The depressions of the NH₄Cl-H₂O (I) and KNO₃-H₂O (II) eutectics lead to the mol. formulæ Na₂S₂O₈ and (NH₄)₂S₂O₈ (I) and K₂P₂O₆ and Na₂H₂P₂O₆ (II). Hydrolysis of K₂S₂O₅ takes place very rapidly with formation of KHSO₃. The data also show that Na₂S₂O₄ is slowly hydrolysed to Na₂S₂O₃+NaHSO₄.

B. W. B.

Apparent molal expansibility of electrolytes and coefficient of expansibility (thermal expansion) as a function of concentration. F. T. GUCKER, jun. (J. Amer. Chem. Soc., 1934, 56, 1017—1021).—The apparent mol. expansibility is defined as $\phi(E_2) = \alpha V - \alpha_1 V_1$, where V is the vol. of solvent in which 1 mol. of solute is dissolved, V_1 is the vol. of the resulting solution, and α and α_1 are the expansion coeff. of solution and solvent, respectively. $\phi(E_2)$ is a linear function of the vol. concn. for aq. solutions of HCl, LiCl, LiOH, NaCl, KCl, NaOH, and Na₂SO₄. The limiting val. of $\phi(E_2)$ is more positive and the negative slope greater at low temp. and with electrolytes of higher valency.

E. S. H.

Physico-chemical studies of complex acids. XI. Vapour-pressure measurements. R. A. ROBINSON and D. A. SINCLAIR (J.C.S., 1934, 642—645).—The change in v.p. of aq. Na₂O, V₂O₅, Na₂O, WO₃, and Na₂O, MoO₃ with addition of HCl is recorded, and the lowering due to the acid anions calc. Mol. wt. vals. approaching 1000 are obtained in acid solutions, indicating the occurrence of polymerisation.

R. S.

Application of simple centrifuges to the determination of particle size in colloid solutions. M. SCHLESINGER (Kolloid-Z., 1934, 67, 135—142).—A simple way of applying the sedimentation method is described. The theory is worked out and some results with Au sols are given.

E. S. H.

Tyndall light of milk, ferric chloride, and aluminium chloride solutions. T. KATSURAI (Kolloid-Z., 1934, 67, 143—145).—The change of Tyndall effect with concn. has been determined. With FeCl₃ the effect in the red region is increased by electrolytes in the order NaCl < BaCl₂ < AlCl₃. When NH₃ is added slowly to aq. FeCl₃ the effect is observed to increase only in the red region, whilst with AlCl₃ an increase is observed in the red, green, and violet regions before pptn. occurs.

E. S. H.

Gold sols with mixed complexes. F. EIRICH and W. PAULI (Kolloid-Z., 1934, 67, 186—195).—Hydroxo-Au sols (I), prepared by dispersion in dil. NaOH, are flocculated by boiling or by CO₂, whilst chloro-Au sols (II), prepared by dispersion in dil. HCl, are stable under these conditions. (I) can be converted into (II) by adding excess of the HCl, and addition of excess of NaOH converts (II) into (I). In the transitional stages mixed complexes are obtained, having intermediate properties. Sols prepared by dispersing Au in aq. BaCl₂ or MgCl₂ become red on heating and violet again on cooling.

E. S. H.

Emulsification of mercury. L. KREMNEV (Kolloid-Z., 1934, 67, 171—178).—Suspensions of many oxides and sparingly sol. salts stabilise Hg emulsions by forming a solid protective sheath around the particles. A similar effect is observed with typical hydrophilic colloids and with hydrated inorg. colloids in sufficient concn. The emulsions are also stabilised by the chlorides of multivalent metals and by oxidising salts, apparently as a result of forming Hg₂Cl₂ or Hg₂O.

E. S. H.

Application of the photographic method for the investigation of the colloidal state of polonium. I. E. STARIK and M. J. DEJZENROT-MISOVSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 540—546).—The method of determining the true or colloidal character of solutions of radioactive materials by bringing a drop of the solution on to a thin mica sheet above a photographic plate (A., 1928, 810; 1929, 620) is untrustworthy, as it is vitiated by adsorption at the mica surface. The method is actually most suited to the study of the latter phenomenon.

J. W. S.

Electric properties of colloid solutions. IV. Difference between the properties of colloidal acid solutions and acids in true solution. J. MUKHERJEE (Kolloid-Z., 1934, 67, 178—186; cf. A., 1933, 1116).—The behaviour of colloidal H₂SiO₃ and H₂SnO₃ differs from that of mol.-dissolved acids on dilution and on neutralisation, different amounts of strong bases [NaOH, KOH, or Ba(OH)₂] being required. The usual conceptions of degree of dissociation and dissociation const. are not applicable without modification; the size of the particles plays a part.

E. S. H.

Structure viscosity. II. Structure viscosity and flow elasticity in gum arabic sols. W. OSTWALD [with R. AUERBACH, I. FELDMANN, V. TRAKAS, and H. MALSS] (Kolloid-Z., 1934, 67, 211—222; cf. A., 1932, 995).—Structure viscosity has been established in gum arabic sols (5—45%) at 21° and 31°. The structural region is limited to low pressures (< 10 cm. H₂O). Flow elasticity is observed in the structural region, particularly at medium and low concns.

E. S. H.

Osmotic properties of colloidal electrolytes and the Hammarsten effect. P. VAN RYSELBERGHE (J. Physical Chem., 1934, 38, 645—653).—The apparent abnormalities in the measured osmotic pressure of colloidal electrolytes are a logical consequence of applying the Debye-Hückel theory to uni-z-valent electrolytes.

F. L. U.

Diffusion of colloids and colloidal electrolytes; ovalbumin; comparison with ultracentrifuge. J. W. MCBAIN, C. R. DAWSON, and H. A. BARKER (J. Amer. Chem. Soc., 1934, 56, 1021—1027).—Rates of diffusion through porous membranes of const. properties lead to correct vals. of mol. wt. if the observations are made at the isoelectric point or, with less certainty, in presence of buffers. Under these conditions the method is rapid and accurate for approx. spherical particles larger than sucrose. Experiments described with ovalbumin indicate mol. wt. 34,000. With insufficient buffering or beyond the isoelectric point widely divergent results may result from the mutual acceleration and retardation of ions and charged particles.

E. S. H.

Conditions for mechanical coagulation. W. HELLER (Compt. rend., 1934, 198, 1776—1778).—Hydrophilic sols coagulate on shaking or stirring, provided that the ζ potential is correctly adjusted. The extent of coagulation varies with the rates of shaking or stirring. It is claimed that all sols can be mechanically coagulated under appropriate conditions (cf. A., 1932, 119).

B. W. B.

Kinetics of coagulation. N. V. KARAKAR and A. M. PATEL (Trans. Faraday Soc., 1934, 30, 493—496).—The coagulation-time curves of $\text{Th}(\text{OH})_4$ sol in presence of KCl , MgCl_2 , and AlCl_3 are S shaped, but with progressive dialysis the auto-catalytic character of the curves disappears. Multivalent cations give a more pronounced S shape to the curves than univalent cations, owing to their greater stabilising influence.

R. S. B.

Soya-bean lecithin. III. Coagulation of lecithin sol by electrolytes. T. IGUCHI and M. SATO (J. Soc. Chem. Ind. Japan, 1934, 37, 198—199B).—The η (Couette) of the sol (2 g. per 100 c.c.) decreases on the addition of electrolytes, giving a min. val. at the end-point of coagulation, which can be more accurately determined by this means than by visual observation. The lecithin particles are negatively charged in colloidal solution, and the coagulation val. decreases with increased valency of the cations of the electrolyte.

E. L.

Influence of dialysis and ebullition on the stability of copper ferrocyanide and arsenic sulphide sols towards some electrolytes. A. BOVTARIC and F. MORIZOT (Bull. Soc. chim., 1934, [v], 1, 153—156).— $\text{Cu}_2\text{Fe}(\text{CN})_6$ hydrosols become progressively less stable towards the coagulating action of KCl on dialysis, but more stable towards BaCl_2 and AlCl_3 , whereas As_2S_3 sols become more stable towards KCl and less stable towards BaCl_2 and AlCl_3 . Increase of the particle size by boiling $\text{Cu}_2\text{Fe}(\text{CN})_6$ sols make them progressively less stable towards all three precipitants, whilst with As_2S_3 sols the stability towards KCl and BaCl_2 is first increased and then diminished and towards AlCl_3 is practically unaffected.

J. W. S.

Stabilising and protective effect of colloidal hydroxides of tervalent metals on mineral suspensions. L. V. LJUTIN and G. V. ZACHAROVA (Kolloid-Z., 1934, 67, 222—229).—Sols of $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$, and $\text{Cr}(\text{OH})_3$ have a protective effect on suspensions of graphite, BaSO_4 , SiO_2 , and glass.

E. S. H.

Influence of the electric field on silver chromate precipitations in gelatin. M. KÖHN (Kolloid-Z., 1934, 67, 207—210).—When AgNO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ interdiffuse in gelatin between two electrodes, the region in which the reagents meet is free from ppt., but the ppt. extends on each side towards the electrodes. A periodic structure is formed on the cathode side. The effects of varying the p.d. are described.

E. S. H.

Silicic acid gels. IV. Effect of hydrogen-ion concentration on time of setting. C. B. HURD, C. L. RAYMOND, and P. S. MILLER (J. Physical Chem., 1934, 38, 663—674; cf. A., 1933, 462).—The time of setting (t) \propto $[\text{H}^+]$ between p_{H} 4.2 and 5.5 for gels made from Na silicate and HCl , and approx. so for those made with AcOH between p_{H} 4.14 and 6.0. Increasing amounts of AcOH and NaOAc at const. p_{H} increase t , whilst NaCl , NaNO_3 , and Na_2SO_4 decrease it without appreciably changing the p_{H} .

F. L. U.

Laws of soil colloidal behaviour. XIV. Ageing of colloids and base exchange. A. J. PUGH (Soil Sci., 1934, 37, 403—427; cf. B., 1934, 32).—Freshly prepared sols of $\text{Al}(\text{OH})_3$ and Al silicate are stable towards $\text{Ba}(\text{OAc})_2$. After 3 weeks there is a decrease in adsorptive capacity and $\text{Ba}(\text{OAc})_2$ causes flocculation. A form of continuous polymerisation of the clay complex is postulated in which the $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratio is unaffected, but rearrangement of internal bonding of the mols. permits fewer mols. to participate in base-exchange phenomena.

A. G. P.

Ion interchanges in chromium oxychloride hydrosols. F. C. VON WICKLEN (J. Amer. Leather Chem. Assoc., 1934, 29, 194—232).—The p_{H} val. of basic CrCl_3 hydrosols is increased by the addition of K salts but diminished by ageing or heating, and reverts slightly when the heated hydrosols are subsequently allowed to remain at room temp. The p_{H} of heated hydrosols is not affected so much by additions of K salts as is that of the sols before heating. The effect of K salts on p_{H} diminishes in the order: $\text{C}_2\text{O}_4''$, citrate, tartrate, OAc' , SO_4'' , CNS' , Cl' , NO_3' . The conductivity of the hydrosols is slightly increased by small additions of AgNO_3 , but diminished very much by Ag_2SO_4 .

D. W.

Swelling capacity of cellulose acetate films. I. D. KRÜGER (Paint and Var. Prod. Man., 1934, 10, No. 6, 22—23).—Published data concerning the influence of the degree of acetylation and of the polarity of the solvent on the swelling of cellulose acetate films are reviewed.

D. R. D.

Rate of flow of cellulose acetate solution. M. NEGISHI (J. Soc. Chem. Ind. Japan, 1934, 37, 133—134B).

A. G.

Intracellular swelling of graphitic acid. I. Isotherms. Influence of lyotropic substances, temperature, and p_{H} on maximum swelling. J. C. DERKSEN and J. R. KATZ (Rec. trav. chim., 1934, 53, 652—669).—During the swelling of graphitic acid in H_2O vapour the distance (D) between adjacent ring-planes increases from 6.02 to 11.31 Å. Absorption of H_2O is therefore intracellular. The max. swelling increases with lowering of temp. and with increase of p_{H} . In 2M solution the effect of Li salts in increasing D is in the order $\text{NO}_3' > \text{CNS}' > \text{ClO}_3' > \text{Br}' > \text{Cl}' > \text{SO}_4''$. EtOH and tannic acid inhibit swelling.

F. L. U.

Existence of micelles in aqueous solutions of saponin. W. KLEINBERG (Proc. Soc. Exp. Biol. Med., 1933, 31, 113—114).—In aq. saponin min. surface tension occurs at concns. 1 in 12,500, 24,500, and 37,500, for which calc. vals. of the mol. dimensions are, respectively, 6.3, 3.2, and 2.1×10^{-6} cm., which are about 10 times the expected vals. Hence agglomerates must be capable of orienting themselves in three different ways, corresponding with their three dimensions.

CH. ABS.

Physical chemistry of proteins. XI. Amphoteric properties of zein. E. J. COHN, J. T. EDSALL, and M. H. BLANCHARD (J. Biol. Chem., 1934, 105, 319—326).—Electrometric titration of zein in 80% EtOH solution shows that it takes up approx. 20×10^{-5} mols. of HCl per g. The dissociation curve

corresponds with $pK_1=5.4$ and $pK_2=6.9$, the change taking place at approx. p_H 8. C. G. A.

Properties of proteins as a function of their fine structure. S. J. VON PRZYŁECKI and M. Z. GRYNBERG (Biochem. Z., 1934, 270, 203—218; cf. A., 1933, 125).—Ovalbumin (I) is adsorbed from aq. solutions of varying p_H in large amounts at the surface of org. liquids, whilst gelatin is adsorbed only slightly or not at all, the extent of adsorption depending on the structure of the protein and on the polar nature of the liquid. Addition of salts (Na_2SO_4 , $MgCl_2$) increases adsorption. With alcohols [except amyl (II)] there is no adsorption. Addition of (II), EtOH, or $COMe_2$ to (I) solutions greatly decreases adsorption. W. McC.

Cryolysis and bio-technology. F. F. NORD (Chem.-Ztg., 1934, 58, 327—328, 347—349).—A comparison of the physical properties of solutions of ovalbumin, gelatin, gum arabic, saponin, and Na oleate and of emulsions of olive oil in the above solutions before and after cooling to -10° , -18° , -79° , and -180° suggests that cooling diminishes the degree of aggregation in dil. solutions, but that the reverse may occur in more conc. solutions. A. G.

Complex relationships in lyophilic colloidal systems. III. (a) Complex and autocomplex flocculi. (b) "Salt solubility" of globulins at the isoelectric point. H. G. B. DE JONG, W. A. L. DEKKER, and K. C. WINKLER. IV. Influence of neutral salts on the cataphoretic charge of suspended (auto-)complex coacervate drops and of (auto-)complex flocculi. H. G. B. DE JONG and J. L. L. F. HARTKAMP (Rec. trav. chim., 1934, 53, 607—621, 622—642; cf. this vol., 362).—III. Examples of autocomplex flocculation are given. Certain systems can be made to exhibit both flocculation and coacervation by suitably controlling the factors determining the mutual relation of the attraction between oppositely charged groups and the tendency to solvation. The solubility of globulins in salt solutions at the isoelectric point is due to the diminution of the opposite charges by the salt ions, with the consequent dominance of the solvation factor. The peptising capacity of salts increases with the valency of either ion.

IV. The cataphoretic charge of drops and flocculi in a no. of complex and autocomplex systems shows a progressive change by salts in the order 1—3, 1—2, 1—1, 2—1, 3—1, the pairs of figures representing the respective valencies of cation and anion. F. L. U.

Action of alkaline copper solution on silk fibroin. IX. Chemical reactions and dissolution phenomena in the system fibroin-copper-alkali. X. Application of conductometric titration methods to the system fibroin-copper-alkali. Y. TAKAMATSU and S. NOMURA (J. Soc. Chem. Ind. Japan, 1934, 37, 149—150B, 150B).—IX. The dissolution of fibroin in $Cu(OH)_2$ -alkali mixtures is accelerated by substances which dissolve $Cu(OH)_2$ without alkali hydroxide (NH_3 , diamines, hydroxy-alkylamines, biguanidine) or in the presence of alkali hydroxide (NH_2 -acids, polyhydroxy-compounds). Their activities are in the same order as their

capacities for dissolving $Cu(OH)_2$, i.e., $C_2H_4(NH_2)_2 >$ tri- and di-(hydroxyethyl)amine $>$ glycine $>$ $NH_3 >$ glycerol. A complex compound [fibroin $Cu_{0.4}$]K has been isolated.

X. Conductometric titration gives quant. separation of free and combined alkali and reveals the existence of the compounds [fibroin $Cu_{0.4}$]M and [fibroin Cu]M, where M is K, Na, or Li. A. G.

Physico-chemical measurements on hydrogen fluoride. II. K. FREDENHAGEN [with W. KLATT, H. KUNZ, and (FRL.) U. BUTZKE] (Z. anorg. Chem., 1934, 218, 161—168).—The isotherms of the vapour at 26° , 32° , and 38° , lead to 86.3, 2.47, and $9.49 (\times 10^{14})$ for the dissociation const. of $(HF)_6$. From the heat of vaporisation at reduced pressure the calc. heat of dissociation of 20 g. of the saturated polymerised vapour is 6020 g.-cal. The saturated vapour of HF at b.p., under atm. pressure, corresponds with $(HF)_{3.5}$. M. S. B.

Hydration of unsaturated compounds. II. Equilibrium between isobutene and tert.-butyl alcohol and free energy of hydration of isobutene. W. F. EBERZ and H. J. LUCAS (J. Amer. Chem. Soc., 1934, 56, 1230—1234; cf. this vol., 369).—The equilibrium between Bu^tOH (I), H_2O , and $CH_2=CMe_2$ (II) has been measured in 0.2N- HNO_3 and 0.1N- $HNO_3 + 0.1N-KNO_3$, starting with (I). The equilibrium const. (K_e) at $\mu=0.2$ is 7.48×10^3 at 25° and 3.94×10^3 at 35° . The rate of dehydration of (I) at $\mu=0.2$ is calc. from K_e and the rate of hydration of (II) (*loc. cit.*), and is found to be \propto to the concn. of acid. The ratio k_{35}/k_{25} is 6.73 and the heat of activation is 34.82 kg.-cal. per mol. H. B.

Equilibria between the possible tautomeric forms of hydrogen peroxide in aqueous solution. [Blackening of cupric hydroxide.] A. QUARTAROLI (Gazzetta, 1934, 64, 243—247; cf. A., 1925, ii, 806).—The mechanism of the blackening of $Cu(OH)_2$ by H_2O_2 has been studied in greater detail. Pure pptd. $Cu(OH)_2$ does not blacken on keeping under H_2O in complete absence of H_2O_2 . Although low concns. of H_2O_2 produce blackening, higher concns. completely inhibit it. It is suggested that in the first case Cu_2O_3 is formed by the action of $H_2O:O$, and reacts with $Cu(OH)_2$ forming the black compound ($\alpha CuO, H_2O$) and H_2O_2 , a chain reaction being thus set up, whereas in the second case CuO_2 is formed by the action of $HO \cdot OH$ and is incapable of further reaction. The negative catalysts Mg^{++} , Co^{++} , and Ni^{++} break the chain by forming compounds of the spinel type, e.g., $Cu_2O_3 \cdot MgO$. D. R. D.

First dissociation constant of phosphoric acid from 0° to 50° . L. F. NIMS (J. Amer. Chem. Soc., 1934, 56, 1110—1112).—The data obtained conform closely with the empirical equation of Harned and Embree (see below) for the dissociation of weak acids and bases. The heat of ionisation is given by $\Delta H = -4.58 \times 10^{-4} T^2 (T - 255.1)$ g.-cal. E. S. H.

Ionisation constant of formic acid from 0° to 60° . H. S. HARNED and N. D. EMBREE (J. Amer. Chem. Soc., 1934, 56, 1042—1044).—The following data have been obtained from e.m.f. measurements of the cells $H_2 | HCO_2H(m_1), HCO_2K(m_2), KCl(m_3) |$

AgCl|Ag: ionisation const., $\log K = -(173.624/T) + 17.88348 \log T - 0.0280397T - 39.06123$; heat of ionisation, $\Delta H = 794.972 + 35.5613T - 0.12838T^2$; difference in sp. heats of reactants and resultants, $\Delta C_p = 35.561 - 0.25679T^2$. E. S. H.

Temperature variation of ionisation constants in aqueous solutions. H. S. HARNED and N. D. EMBREE (J. Amer. Chem. Soc., 1934, 56, 1050—1053).—In aq. solution at 1 atm. the ionisation const. of weak acids, bases, and ampholytes can be represented by $\log K - \log K_m = f(t-0)$, where $f(t-0)$ is a general function, and K_m is the max. val. of K at the temp. 0. The approx. equation $\log K - \log K_m - 5.0 \times 10^{-5}(t-0)^2$ is valid in the region near the max. val. of K . The change in heat content of ionisation is given by $\Delta H = 2.3RT^2[\partial f(t-0)/\partial T]$. E. S. H.

Constitution of homogeneous acids and the influence of solvents on their acidity. A. MÜLLER (Z. anorg. Chem., 1934, 218, 210).—Corrections relative to a previous paper (this vol., 489).

M. S. B.

Apparent dissociation constants of amino-acids and related substances in water-ethanol mixtures. T. H. JUKES and C. L. A. SCHMIDT (J. Biol. Chem., 1934, 105, 359—371).—EtOH depresses the dissociation of CO_2H groups and slightly increases that of $\alpha\text{-NH}_2$ groups, in agreement with the zwitter-ion theory. The effect of glycerol and mannitol on glycine is slight.

C. G. A.

Hydrolysis of sodium aluminate. A. MAFFEI (Gazzetta, 1934, 64, 149—160).—From the conductivity of solutions of Na aluminate containing varying quantities of NaOH, the hydrolysis const. is found to be 1.66×10^{-3} , and the dissociation const. of $\text{Al}(\text{OH})_3$ as a monobasic acid, 6×10^{-12} . O. J. W.

Activity and osmotic coefficients of aqueous solutions of acetic acid at the m.p. P. VAN RYSELBERGHE (Bull. Acad. roy. Belg., 1934, [v], 20, 354—358; cf. this vol., 490).—Methods of calculation and tabulated results are given.

N. M. B.

Activity of zinc chloride solutions. L. BRÜLL (Gazzetta, 1934, 64, 261—270).—The activity coeffs. of ZnCl_2 calc. from e.m.f. measurements with the cell $\text{Zn}-\text{Hg}|a\text{q. ZnCl}_2|\text{HgCl}|\text{Hg}$ at 25° (concn. of ZnCl_2 0.0017—0.84M) agree with Bonino's theory (this vol., 254).

D. R. D.

Activity coefficient of hydrochloric acid in cerous chloride solutions at 25° . C. M. MASON and D. B. KELLAM (J. Physical Chem., 1934, 38, 689—692).—The activity coeff. of HCl in aq. CeCl_3 determined by e.m.f. measurements at 25° is given by $\log \gamma = 0.0740m - 0.1619$, where $m = [\text{HCl}]$ in mol. per kg. H_2O , and when the const. ionic strength $= 1 \mu$.

F. L. U.

Beryllium tartrate. I. PEYCHÈS (Compt. rend., 1934, 198, 1778—1781; cf. this vol., 718).—Rotatory powers (I) of solutions containing different mol. proportions of BeSO_4 and tartaric acid give max. corresponding with $\text{C}_4\text{H}_4\text{O}_6\text{Be}_2$. Measurements of (I), rotatory dispersion (II), Λ , p_{H} , d , and n have been made for Be_2 tartrate solutions over a wide concn.

range. (I) and (II) are considerably $>$ those for alkali or alkaline-earth tartrates, and vary little with the concn. (I) is attributed chiefly to $\text{C}_4\text{H}_4\text{O}_6\text{Be}^-$.

B. W. B.

Behaviour of the magnesium ion towards ammonia in aqueous solution. II. Determination of the vapour pressure of ammonia over ammoniacal solutions of magnesium salts. H. FREDHOLM (Z. anorg. Chem., 1934, 218, 169—180).—In a dynamical method for the determination of the v.p. of NH_3 over its solution the gas stream is supplied by a H_2O voltameter and the amount of gas passed is measured by a Ag coulometer. Data are given for the following solutions: 1.627N- NH_4Cl , 1.348N- NH_3 , and 0—1.300N- MgCl_2 ; 1.588N- NH_4NO_3 , 1.329N- NH_3 , and 0—1.201N- $\text{Mg}(\text{NO}_3)_2$. By the application of Henry's law the concns. of combined and uncombined NH_3 in solution have been calc. These vals. have been corr. for the salting-out effect of MgCl_2 and $\text{Mg}(\text{NO}_3)_2$ on NH_3 by determining experimentally the salting-out effect of KCl and KNO_3 and assuming that equiv. quantities of salts have the same action. The complex ion $[\text{Mg}(\text{NH}_3)]^+$ is indicated (cf. this vol., 484).

M. S. B.

Determination of calcium-ion concentration and its application to the determination of the dissociation of calcium hydroxide. G. KILDE (Z. anorg. Chem., 1934, 218, 113—128).—The solubility product of $\text{Ca}(\text{IO}_3)_2$ and its variation with temp. and salt concn. have been determined in neutral aq. KIO_3 , CaCl_2 , NaCl , and MgCl_2 , and formulæ are given for the variation of activity coeff. with ionic strength. The solubility of $\text{Ca}(\text{IO}_3)_2 \cdot 6\text{H}_2\text{O}$ in alkaline solution is considerably $>$ in neutral solutions of the same ionic strength. This is attributed to the reaction $\text{Ca}(\text{H}_2\text{O})_6^{++} = \text{Ca}(\text{H}_2\text{O})_5\text{OH}^+ + \text{H}^+$, and may be employed for the determination of the second dissociation const. of $\text{Ca}(\text{OH})_2$. From the solubility in HCl the dissociation const. of HIO_3 has been obtained at 18° , 25° , and 30° , and the vals. are in good agreement with those found by conductivity measurements. From the solubility of CaIO_3 in CaO -sucrose solutions $[\text{Ca}^{++}]$ is considerably $<$ the total $[\text{Ca}]$.

M. S. B.

Mathematical treatment of base-carbonic acid-water equilibria in dilute solutions. Y. KAUKO (Suomen Kem., 1934, 7, 86B).—Relations based on the classical dissociation theory are also valid on the modern theory if K is considered as a function of the concn.

S. C.

Acid strength of inorganic cations and basic strength of inorganic acetates in acetic acid. II. I. M. KOLTHOFF and A. WILLMAN (J. Amer. Chem. Soc., 1934, 56, 1014—1016).—The dissociation of inorg. acetates in AcOH decreases with decreasing size and increasing charge of the cation. The acid strength of the cation increases with decreasing size and increasing charge. Salts which do not change the reaction of H_2O undergo solvolysis in AcOH. The acidity of K salts decreases in the order $\text{ClO}_4^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{NO}_3^-$. Salts of the same anion decrease in acidity in the order $\text{Mg}^{++} > \text{Ca}^{++} > \text{Sr}^{++} > \text{Ba}^{++} (> \text{Ag}^+) > \text{Li}^+ > \text{Na}^+ > \text{NH}_4^+ = \text{K}^+ > \text{Rb}^+$. Glycine behaves as a strong base.

E. S. H.

Hydration of solute ions in relation to acidity, alkalinity, and p_{H} . L. H. FLINT (Plant Physiol., 1934, 9, 107—126). A. G. P.

Theory for concentrated solutions of strong electrolytes. L. BRÜLL (Gazzetta, 1934, 64, 270—278).—The fundamental differences between Bonino's theory (this vol., 254) and the Debye-Hückel theory are examined. A simple interpolation formula for calculating f^* is obtained and shown to give the same vals. (within 1%) as Bonino's more complicated theoretical formula in the case of 0.2—3*M*-KCl, 0.01—5.41*M*-NaCl, and 0.01—1*M*-CaCl₂, -SrCl₂, and -BaCl₂ at 25°. D. R. D.

Diffusion equilibria of electrolytes. O. HALPERN (J. Chem. Physics, 1934, 2, 300).—Diffusion equilibrium under the influence of external forces, illustrated by the distribution of charged colloidal particles and ions in a gravitational field, shows deviations from the Boltzmann distribution; the diffusion potential of electrolytes does not assume its classical val. N. M. B.

Activities of life and the second law of thermodynamics. F. G. DONNAN and E. A. GUGGENHEIM (Nature, 1934, 133, 869; cf. this vol., 598). L. S. T.

Statistical thermodynamics of molecular systems. T. WEREIDE (Z. Physik, 1934, 88, 469—494).—The criterion of thermodynamic equilibrium, $d\delta S=0$, is combined with a statistical calculation of entropy, S , so that quantum conditions appear only in empirically determined coeffs. The method is applied to the principal types of thermodynamical processes, including evaporation, fusion, absorption, osmosis, chemical reactions, and electrode potentials. A. B. D. C.

Graphical calculations in the study of chemical equilibria. P. MONTAGNE (Chim. et Ind., 1934, 31, Spec. No., 204—209).—Applications of graphical methods are reviewed. H. J. E.

Thermal dissociation of lead peroxide. J. KRUSTINSONS (Z. Elektrochem., 1934, 40, 246—248).—The dissociation pressure of PbO₂, dried in a current of O₂ at 250°, is 1 atm. at 344±1°. The calc. heat of dissociation is 21,670 g.-cal. The end product is PbO, but solid solutions are formed in the earlier stages. E. S. H.

V.p.-temperature relations and the heats of hydration, dissolution, and dilution of the binary system magnesium nitrate-water. W. W. EWING, E. KLINGER, and J. D. BRANDNER (J. Amer. Chem. Soc., 1934, 56, 1053—1057).—V.p. measurements are recorded for solutions, and for the hydrates of Mg(NO₃)₂. Heats of dissolution and dilution have also been measured and heats of hydration calc. from the results and from the v.-p. data. E. S. H.

System sodium nitrite-water. The hydrate NaNO₂·0.5H₂O. J. BUREAU (Compt. rend., 1934, 198, 1918—1920).—Recorded data show the existence of NaNO₂·0.5H₂O with a eutectic at -19.5° and 28-10% NaNO₂, and transition point hemihydrate → anhyd. salt at -5.1° and 41.65%. Vals. of d for saturated NaNO₂ solutions are tabulated between 15° and 99.9°. B. W. B.

Binary system lithium nitride-water. A. P. ROLLET and J. WOHLGEMUTH (Compt. rend., 1934, 198, 1772—1774).—An equilibrium diagram is given, showing a eutectic (I) (-47.5°, 26.0% LiN₃) and two transition points, (II) (-31.0°, 33.5%) and (III) (68.2°, 48.0%). LiN₃·4H₂O separates between (I) and (II), and LiN₃·H₂O between (II) and (III). B. W. B.

M.-p. diagram of the system ZrO₂-SiO₂. N. ZIRNOVA (Z. anorg. Chem., 1934, 218, 193—200).—The system gives a max. m.p. at 2430° for the 50% mol. mixture, indicating the presence of the compound ZrSiO₄. There are two eutectics, 2220°, 42 mol.-% SiO₂; 1705°, 97 mol.-% SiO₂. The region of solid solutions lies between 10 and 100 mol.-% SiO₂. M. S. B.

Dissociation pressures of metal pyridine cyanates. T. L. DAVIS and C. W. OU (J. Amer. Chem. Soc., 1934, 56, 1061—1063).—Data are recorded for Co(NCO)₂, 2, 4, and 6C₅H₅N, Ni(NCO)₂, 4 and 6C₅H₅N, and Zn(NCO)₂, 2C₅H₅N at 20—100°. C₅H₅N is bound by Ni(NCO)₂ and Zn(NCO)₂ less strongly at the lower temp. The dissociation of Co(NCO)₂, 6C₅H₅N in boiling CHCl₃, and of Co(NCO)₂, 6C₅H₅N and Co(NCO)₂, 4C₅H₅N in Ph₂ solution at about 68° has been measured. E. S. H.

Thermal analysis of binary systems of resorcinol and sulphur with certain organic substances. K. HRYNAKOWSKI and F. ADAMANIS (Rocz. Chem., 1934, 14, 189—196).—The fusion diagrams suggest 1:1 compounds in the systems *m*-C₆H₄(OH)₂ (I)-antipyrine (II), CO(NH₂)₂ (III), but not in the systems (I)-BzOH, NHPH₂ (IV), *p*-C₆H₄(OH)₂ (V), salol (VI), NH₂Et-CO₂Et (VII), or S-(IV), α-C₁₀H₇·NH₂, quinine. S is immiscible with fused NHAcPh, (II), (III), *p*-OEt·C₆H₄·NHAc, (V), menthol, (VI), and (VII). R. T.

Molecular compounds of the chalkones and nitro-aromatic compounds. T. ASAHINA (Bull. Chem. Soc. Japan, 1934, 9, 181—186).—M.-p. diagrams are given for the systems *o*-C₆H₄Me·NO₂-3:4-methylenedioxybenzylideneacetophenone (I) [simple eutectic (S.E.)]; *o*-OH·C₆H₄·NO₂ (II)-benzylideneacetophenone (III) (S.E.); (I)-(II) (S.E.); *m*-OH·C₆H₄·NO₂ (IV)-(III), (compound, 1 mol.:1 mol., m.p. 65°); (IV)-(I) (compound, 1:1, m.p. 96.5°), *p*-OH·C₆H₄·NO₂ (V)-(I) (compound, 1:1, m.p. 109.0°); (V)-(III) (compound, 1:1, m.p. 87°). D. R. D.

Heterogeneous equilibrium in the system CdCl₂-NaCl-H₂O. (MLLE.) M. G. ADOLFF and H. HERING (Compt. rend., 1934, 198, 1770—1772).—Data for the range 19.3—60.0° indicate the existence of CdCl₂·2NaCl·3H₂O (I) (cf. Käthe, A., 1914, ii, 205), 5CdCl₂·4NaCl·17H₂O, and CdCl₂·NaCl·H₂O. (I) exists at all temp. B. W. B.

Mixed crystals in the vitriol series. III. System NiSO₄-CoSO₄-H₂O. A. BENRATH and W. THEMANN (Z. anorg. Chem., 1934, 217, 347—352; cf. this vol., 137).—Equilibrium diagrams have been constructed showing the regions of formation of mixed crystals of the respective mono-, hexa-, and heptahydrates of Co and Ni. Hexahydrate crystals contain the Ni salt in the β form. F. L. U.

Ternary systems. XIX. Calcium sulphate, potassium sulphate, and water. A. E. HILL (J. Amer. Chem. Soc., 1934, 56, 1071—1078).—Equilibrium data for the range 40—100° show that the separation of K_2SO_4 from $CaSO_4$ in natural polyhalite is not appreciably favoured by rise of temp., and that the concn. of K_2SO_4 may increase as a result of the metastable pptn. of anhydrite. E. S. H.

Isotherms of the ternary system P_2O_5 — Li_2O — H_2O at 0° and 20°. A. P. ROLLET and R. LAUFFENBURGER (Bull. Soc. chim., 1934, [v], 1, 146—152).—The only compounds formed are Li_3PO_4 and LiH_2PO_4 , the latter of which has an incongruent solubility at 20°. The solubilities at 0° are 0.022% and 55.8%, respectively, and that of Li_3PO_4 at 20° is 0.030%. J. W. S.

Acid salts in systems of the type monobasic acid-alkaline-earth salt-water. L. J. DUNN and J. C. PHILIP (J.C.S., 1934, 658—666; cf. A., 1928, 131).—For HCO_2H , $AcOH$, $PhSO_3H$, and their Ba, Sr, Ca, and Mg salts the following solid phases are indicated: (1) $(HCO_2)_2Ba$; $(HCO_2)_2Ba.HCO_2H$; ternary point, 21.8 HCO_2H , 26.7 $(HCO_2)_2Ba$, 51.5% H_2O ; (2) $(HCO_2)_2Sr.2H_2O$; $(HCO_2)_2Sr$; $2(HCO_2)_2Sr.HCO_2H$; ternary points, 55.9 HCO_2H , 20.0 $(HCO_2)_2Sr$, 24.1% H_2O , and 68.7 HCO_2H , 21.3 $(HCO_2)_2Sr$, 10% H_2O ; (3) $(HCO_2)_2Ca$; (4) $(HCO_2)_2Mg.2H_2O$; (5) $3Ba(OAc)_2.3AcOH.11H_2O$; (6) $2Sr(OAc)_2.H_2O$; $5Sr(OAc)_2.5AcOH.9H_2O$; $Sr(OAc)_2.2AcOH.2H_2O$; (7) $Ca(OAc)_2.H_2O$; $Ca(OAc)_2.AcOH.H_2O$; ternary point, 7.6 $AcOH$, 25.1 $Ca(OAc)_2$, 67.3% H_2O ; (8) $(PhSO_3)_2Ba.H_2O$; (9) $(PhSO_3)_2Sr.H_2O$; (10) $(PhSO_3)_2Ca.H_2O$; (11) $(PhSO_3)_2Mg.6H_2O$. The solubilities of $(HCO_2)_2Ba$ and $(HCO_2)_2Sr$ increase with the acid concn. All others decrease. R. S.

Equilibrium between binary compounds and the associated metals. H. GIERSCH (Metallbörse, 1933, 23, 893—894; Chem. Zentr., 1933, ii, 2935).—The mass-action law of Lorenz and van Laar holds for equilibria of the type $Pb+SnCl_2=PbCl_2+Sn$. H. J. E.

Equilibria between metals, sulphides, and silicates in the melt. IV. Heterogeneous equilibrium $FeS+Ni$ silicate $=NiS+Fe$ silicate in the melt. W. JANDER, H. ZWEYER, and H. SENF (Z. anorg. Chem., 1934, 217, 417—426; cf. A., 1933, 352).—Data are recorded to show the influence of concn., temp., and additions of foreign substances on the equilibrium. F. L. U.

Phase diagrams of simultaneous crystallisation of sodium chloride and epsomite. V. I. NIKOLAEV and N. P. VINTOVKINA (J. Appl. Chem. Russ., 1934, 7, 29—38).—Data for the system $2NaCl+MgSO_4=Na_2SO_4+MgCl_2$ at 0—48° are recorded, and the results discussed with reference to conditions prevailing in a no. of U.S.S.R. salt lakes. R. T.

Combination of amino-acids and proteins in the solid state with gaseous acids and bases.—See this vol., 790.

Thermochemistry of aqueous solutions of nickel sulphate. J. PERREU (Compt. rend., 1934, 198, 1767—1769; cf. this vol., 601).—Heats of dissolution of $NiSO_4.7H_2O$ together with sp. heats of

solutions and heats of dilution are recorded. The results give calc. vals. in good agreement with Steele and Johnson's data for the eutectic temp. and the transition temp. for the changes hepta- \rightarrow hexahydrate and $\alpha \rightarrow \beta$ hexa-hydrate (J.C.S., 1904, 85, 113). B. W. B.

Heats of dissolution of calcium oxide and calcium hydroxide in relation to concentration of hydrochloric acid. H. E. SCHWIETE and E. HEY (Z. anorg. Chem., 1934, 217, 396—400).—Heats of dissolution have been measured for 1, 3.5, and 6.4*N*-HCl. The calc. heat of hydration of CaO is 15.55 kg.-cal. per mol. F. L. U.

Thermochemistry of ferrous halides and their compounds with carbon monoxide. W. HIEBER and A. WOERNER (Z. Elektrochem., 1934, 40, 287—291).—The following thermal data have been determined: $Fe+Br_2$ (liquid) $=FeBr_2+59.87$, $Fe+I_2$ (solid) $=FeI_2+30.12$ kg.-cal.; $Fe(CO)_5+X_2$ (gas) $=Fe(CO)_4X_2+CO+45.84$ (Cl), 43.38 (Br), 23.14 kg.-cal. (I). Thermal data relating to the system $Fe-CO-X$ are now complete, and independently calc. vals. show a satisfactory agreement. F. L. U.

Heats of formation and constitution of ferrous halide compounds with amines and carbon monoxide. W. HIEBER, H. APPEL, and A. WOERNER (Z. Elektrochem., 1934, 40, 262—267).—Data are recorded for the complexes formed by $FeCl_2$, $FeBr_2$, and FeI_2 with C_5H_5N , $C_2H_4(NH_2)_2$, and CO, respectively, and are discussed in relation to constitution. The prep. of the following compounds is described: $FeCl_2.3C_2H_4(NH_2)_2$, $FeBr_2.4C_5H_5N$, $FeBr_2.6C_5H_5N$, $FeBr_2.3C_2H_4(NH_2)_2$, $FeI_2.2C_5H_5N$, $FeI_2.4C_5H_5N$, $FeI_2.6C_5H_5N$, $FeI_2.3C_2H_4(NH_2)_2$. E. S. H.

Heats of formation and constitution of complex cobaltous halide compounds. II. W. HIEBER and A. WOERNER (Z. Elektrochem., 1934, 40, 256—262; cf. A., 1930, 421).—The heats of formation of compounds of $CoCl_2$, $CoBr_2$, and CoI_2 with numerous amines and alcohols have been calc. from the heats of dissolution of the complexes and their components in the same solvent. The results are discussed in relation to constitution. E. S. H.

Heats of combustion of cyclic hydrocarbons. G. BECKER and W. A. ROTH (Ber., 1934, 67, [B], 627—632; cf. Alder and Stein, this vol., 517).—The vals. at const. vol. and const. pressure, respectively, are: α -dicyclopentadiene (1376.6, 1378.4), H_2 - (1411.0, 1413.1) and H_4 - (1451.8, 1454.2) -derivatives; α -tricyclopentadiene (2053.1, 2055.8), H_2 - (2088.6, 2091.6) and H_4 - (2132.4, 2135.6) -compounds; β -di- (2086.4, 2089.4) and β -tetra- (2128.7, 2132.0) -hydrotricyclopentadiene; tetracyclopentadiene (2727.3, 2730.8) and its H_2 -compound (2762.2, 2766.0); norcamphor (944.9, 946.1); dicyclohexadiene (1679.1, 1681.5) and its H_4 -compound (1757.9, 1760.9). H. W.

Heats of activation of explosive molecules. H. MURAOUR (J. Chim. phys., 1934, 31, 138—140).—The heat of activation calc. by Roginski and Andreev (A., 1933, 1017) does not refer to the explosive decomp. of 2:4:6-trinitro-1:3:5-triazobenzene and hence

there is no significance in the comparison with activation energies of other explosives (cf. *ibid.*, 574).

J. G. A. G.

Heats of activation of explosive molecules. C. C. ANDRÉEV (J. Chim. phys., 1934, 31, 141—144).—A reply (cf. preceding abstract).

J. G. A. G.

[Heats of activation of explosive molecules.] H. MURAOUR (J. Chim. phys., 1934, 31, 145—146).—A reply (cf. preceding abstract). Activation energies for the slow decomp. of explosives can be calc. from the temp. coeff. only if at the temp. chosen each fraction of the total vol. of gas liberated corresponds with the decomp. of an equal fraction of the explosive.

J. G. A. G.

Visualising and recording the propagation front of ions. R. TOMII (J. Soc. Chem. Ind. Japan, 1934, 37, 166—167B).—By choosing suitable substances, e.g., $K_4Fe(CN)_6$, NaCl, and phenolphthalein, and interrupting the current from time to time the ionic front in a gelatin gel is made visible. With an anode at the centre of a circular cathode the rate of movement of the front is proportional to the c.d.

A. G.

Electrolytic conductivity of alkaline-earth chlorides in water at 25°. T. SHEDLOVSKY and A. S. BROWN (J. Amer. Chem. Soc., 1934, 56, 1066—1074).—Conductivity and d vals. are recorded for aq. $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ solutions at 25°. The conductivity vals. agree with Onsager's equation.

E. S. H.

Azido-dithiocarbonic acid. VII. Conductivity of the azido-dithiocarbonate ion. G. B. L. SMITH, F. P. GROSS, jun., G. H. BRANDES, and A. W. BROWNE (J. Amer. Chem. Soc., 1934, 56, 1116—1118).—Conductivity measurements show $SH \cdot CS \cdot N_3$ to be a moderately strong acid. Potentiometric titration and cryoscopic determinations confirm this result. The equiv. conductivity of $S \cdot CS \cdot N_3'$ at 25° is 41.7.

E. S. H.

Dissociation of inorganic acids, bases, and salts in glacial acetic acid as solvent. I. I. M. KOLTHOFF and A. WILLMAN (J. Amer. Chem. Soc., 1934, 56, 1007—1013).—Conductivity measurements show that the strength of inorg. acids in AcOH decreases in the order $HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$. $HClO_4$ behaves as a strong electrolyte, and is present partly as ions and partly in the form of ion pairs, $CMe(OH)_2 \cdot ClO_4$. The remainder behave as weak acids; they are partly dissociated, partly present as ion pairs, and partly non-ionised. Alkali acetates and LiCl behave as strong electrolytes.

E. S. H.

Potential of iron in air-free solution. F. MEUNIER and O. L. BIHET (Chim. et Ind., 1934, 31, Spec. No., 444—447).—Measurements made in vac. indicate that OH' does not produce passivity. In alkaline solution, however, Fe, Ni, Cr-Ni steel, and polished Pt behave like H electrodes. In acid solution the action depends on the nature and concn. of the ion, CrO_4'' producing passivity, whilst SO_4'' has only a feeble effect.

H. S. P.

Potentials of cells in liquid ammonia solutions. Thermodynamic constants of the ammino-zinc chlorides and of zinc chloride. N. ELLIOTT and D. M. YOST (J. Amer. Chem. Soc., 1934, 56, 1057—

1060).—The e.m.f. of the reversible cells Zn (amalgam), $ZnCl_2, 10NH_3(s) | NH_4Cl$ (in liquid NH_3) | $TlCl(s)$, Tl (amalgam) is const. and reproducible. For unit activity of Zn and Tl in the amalgams the standard potential is $E_{298}^\circ = 0.9016$ volt. For the metals in the free state the standard potential is $E_{298}^\circ = 0.8293$ volt. The free energies, heat contents, and virtual entropies of $ZnCl_2$ and its compounds with 10, 6, 4, 2, and 1 mol. of NH_3 have been calc.

E. S. H.

Behaviour of the glass electrode in connexion with its chemical composition. B. LENGVEL and E. BLUM (Trans. Faraday Soc., 1934, 30, 461—471).—Soft soda-glass containing CaO , Na_2O , and SiO_2 acts as an almost perfect H electrode, with no change in electrometric behaviour when the proportions of the constituents are varied, or when Na_2O is replaced by K_2O . For hard Jena glass containing Al_2O_3 or B_2O_3 the concn. of H' and of alkali metal ion affects the potential. Glasses containing $> 10\%$ Al_2O_3 or B_2O_3 do not differ electrometrically. There is no relation between the behaviour of glass as an electrode and its solubility in H_2O or electrical resistance. The heats of liberation of the migrating ion (Na') have been computed from the temp. dependence of the resistance, but no correlation with electrode phenomena has been found.

R. S. B.

Effect of high concentrations on the deposition potential of polonium. M. GUILLOT and M. HAFSINSKY (Compt. rend., 1934, 198, 1758—1760; cf. A., 1933, 355).—The crit. deposition potential (I) of Po has been measured in various acid and salt solutions. (I) is const. at 0.37 volt in HNO_3 (II) up to 4N, but decreases in H_2SO_4 (III) to 0.10 volt at concns. $> 4N$, and is 0.24 volt in 1-12N-AcOH (IV). In N -(II), -(III), -(IV), and $-H_3PO_4$, (I) decreases with addition of corresponding Na salt. Deposition of Po is suppressed by addition of $K_4Fe(CN)_6$ or $K_3Fe(CN)_6$.

B. W. B.

Electrochemical properties of germanium. J. I. HALL and A. E. KOENIG (Trans. Electrochem. Soc., 1934, 65, 79—82).—Coherent, grey deposits of Ge on Cu are obtained by electrolysis of a solution of GeO_2 in 3N-KOH at 78—90° with low c.d. Measurements of the deposition potential of Ge from this solution, of the single potential of $Ge|N-ZnSO_4$, and of the H overvoltage of Ge are recorded. Ge displaces Ag from aq. $AgNO_3$.

H. J. T. E.

Electrochemical behaviour of the tin-iron couple in dilute acid media. T. P. HOAR (Trans. Faraday Soc., 1934, 30, 472—482).—The e.m.f. of the Fe-Sn couple reverses in dil. acids owing to dissolution of oxide films. Sn is cathodic in H_2SO_4 , but anodic in dil. citric and oxalic acid owing to formation of sol. complexes. Sn and Fe corrode in citric acid and citrate buffer of p_H 5, and when coupled the Sn corrodes more and the Fe less rapidly; there is a quant. relation between the amount of corrosion and the couple current. Air increases the corrosion of the couple, but a change in p_H has no effect. The bearing of these results on the corrosion of Sn-plate is discussed.

R. S. B.

Potentiometric studies of passivity. J. STEINER and L. KAHLENBERG (Trans. Electrochem. Soc., 1934,

66, 1—8).—The variation of single potential of metals in HNO_3 with dilution of the acid has been studied. Fe, Co, Ni, and certain Fe alloys are definitely active and definitely passive over certain ranges of concn. In the region of intermediate concns. periodic phenomena are sometimes observed with partly immersed specimens, but never for totally immersed specimens. Cr and an Fe-Cr alloy were found to be passive at all concns. of HNO_3 . Single potentials for Al, W, Pt, and graphite in solutions up to 83% HNO_3 are also shown by means of curves. H. J. T. E.

Passivity of iron and steel in nitric acid solutions. I. Y. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 375—455).—Vals. are given for the crit. concn. above which passivity occurs, and the crit. temp. for each concn. below which passivity occurs, when soft steel is immersed in 50—95 wt.-% HNO_3 solution. In the crit. regions periodic passivity is observed. From 75—95 wt.-% HNO_3 the steel does not become completely active even in the boiling solution. The influence of the temp. of the test-piece is described. R. S. B.

Electrolytic valve action of niobium and tantalum on a.c. circuits. D. F. CALHANE and A. J. LALIBERTE (Trans. Electrochem. Soc., 1934, 65, 287—293).—Oscillograph records show that in 27% H_2SO_4 Ta exhibits very effective rectifying action at 60 volts a.c., whereas Nb shows very little electrolytic valve action even at 2.5 volts. H. J. T. E.

Reaction velocity measurements with heavy hydrogen. K. F. BONHOEFFER, F. BACH, and E. FAJANS (Z. physikal. Chem., 1934, 168, 313—314).—The reaction of H_3^+ with Br vapour at 578° abs. is "3.3 times as slow" as the reaction with H_2^+ , and there is a comparable relation between the rates of the reaction $\text{H}_3^+ + \text{H}_2^+ = 2\text{H}^+\text{H}^+$ and the para-ortho H_2 transformation, both on Ni (cf. this vol., 156). R. C.

Low-pressure explosion limits of deuterium and oxygen. A. A. FROST and H. N. ALYEA (J. Amer. Chem. Soc., 1934, 56, 1251—1252).—Explosion limits are compared for $\text{H}_2 + \text{O}_2$ and $\text{D}_2 + \text{O}_2$ mixtures at 500° and 520° in KCl-coated Pyrex vessels. E. S. H.

Reaction between oxygen and the heavier isotope of hydrogen. C. N. HINSHELWOOD, A. T. WILLIAMSON, and J. H. WOLFENDEN (Nature, 1934, 133, 836—837).—With H_2^2 the chain reaction which occurs in the gas phase at 560° and pressures > the upper explosion limit (I) has a speed 64% of that shown by H_2^1 . The ratio of the rates for H_2^2 and for H_2^1 is approx. 0.65—0.70 for the surface reaction in a packed vessel at 525°. (I) is higher with H_2^2 than with H_2^1 , and the shift of the limit is practically that predicted from the theory of deactivation by ternary collisions. H_2^2 by reason of its smaller speed is a less efficient deactivating agent. The energy of activation of the branching process is 26,500 g.-cal., which is approx. the same as the vals. 25,500 and 26,500 for H_2^1 . There appears to be little difference in the actual probability of chain branching with the two isotopes. The mechanism of the reaction is discussed in the light of these results. L. S. T.

Thermal decomposition of fluorine monoxide. A unimolecular decomposition represented by a second-order reaction. W. KOBLITZ and H. J. SCHUMACHER (Z. physikal. Chem., 1934, B, 25, 283—300).—The thermal decomp. in glass, quartz, or Mg vessels at 250—270° is homogeneous and unimol. and follows the equation $-d(\text{F}_2\text{O})/dt = k_1[\text{F}_2\text{O}]^2 + k_2[\text{F}_2\text{O}][\text{O}_2] + k_3[\text{F}_2\text{O}][\text{SiF}_4] + \dots + k_x[\text{F}_2\text{O}][\text{X}]$, where $[\text{O}_2]$ and $[\text{SiF}_4]$ are the concns. of O_2 and SiF_4 formed by reaction with the wall of the F_2 formed by decomp., and X is a foreign gas. The temp. coeff. is 2.0 ± 0.1 and is the same for $k_1, k_2, k_3, \dots, k_x$. Although the decomp. of the F_2O is unimol., the life of the activated F_2O mols. is so short that under the experimental conditions the rate of decomp. is determined by the rate of activation of activated mols. necessary for decomp. Assuming three activated degrees of freedom, there must be complete equalisation of energy at practically every collision, and every mol. with the requisite energy must decompose. The relative probabilities of activation on collision of F_2O and various foreign gases have been calc. The life of the activated F_2O is estimated at $< 10^{-12}$ sec.; the products of dissociation are uncertain. R. C.

Kinetics of ethylene polymerisation. M. V. KRAUZE, M. S. NEMTZOV, and E. A. SOSKINA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 301—306; cf. A., 1930, 709; 1931, 436).—With high C_2H_4 concns. at temp. $> 300^\circ$ no catalytic action could be detected at the surfaces of Fe, Ni, Cu, Cr, ZnO, or activated C, the homogeneous reaction only occurring. The latter is bimol., but a slight fall of the velocity coeff. occurs with increasing initial concn. of C_2H_4 . The effect of temp. is expressed by $\log K = 10.85 - 8400/T$, and the energy of activation is $37,700 \pm 200$ g.-cal. Comparison of the experimental data with theory shows that only one out of every 400 active contacts leads to reaction. J. W. S.

Chains in the acetaldehyde decomposition.—See this vol., 758.

Double hydrolysis of monochloroacetates and their mutual action. A. TIAN (Bull. Soc. chim., 1934, [v], 1, 115—119; cf. A., 1933, 678).—The abnormal temp. coeff. of the elimination of the Cl, and the fact that this action is much more rapid for the salts than for the free acid, in spite of the fact that addition of HCl has little effect on the reaction, are explained by the normal saline hydrolysis of the salts, yielding OH' ions which activate the Cl hydrolysis. This view also explains previous conflicting data on the temp. coeff. of the reaction. J. W. S.

Calculations of the activation energies of reactions between the halogens and the ethylene double bond. A. SHERMAN and C. E. SUN (J. Amer. Chem. Soc., 1934, 56, 1096—1101).—Theoretical. The mechanism of decomp. of $\text{C}_2\text{H}_4\text{I}_2$, $\text{C}_2\text{H}_4\text{Br}_2$, and $\text{C}_2\text{H}_4\text{Cl}_2$ is discussed. E. S. H.

Velocity and equilibrium point of the reaction of formation of benzanilide from benzoic acid and aniline. E. S. CHOTINSKI, B. Z. AMITIN, and I. Z. CHASKES (Ukrain. Chem. J., 1933, 8, 196—201).—The equilibrium point of the reaction $\text{NH}_2\text{Ph} + \text{BzOH} \rightleftharpoons \text{NHBzPh}$ (I) $+ \text{H}_2\text{O}$ is attained in 15 hr. at

155° [52.5% yields of (I)], and in 5 hr. at 212° (64% yields); the velocity of reaction is in both cases greatest during the first hr. R. T.

Hydrolysis of aqueous alkali cyanides during evaporation. I. M. NOSALEVITSCH (Ukrain. Chem. J., 1933, 8, 226—236).—At atm. pressure boiling *N*-KCN undergoes hydrolysis at the rate of 10% per hr., whilst under reduced pressure % hydrolysis (I) diminishes by 0.32 per 10 mm. pressure. (I) diminishes rapidly with increasing concn. of KCN to 5*N*, above which it falls very gradually. R. T.

Alcoholysis of glyceryl triacetate in feebly alkaline media. E. M. BELLET (Compt. rend., 1934, 198, 1785—1786; cf. A., 1933, 696).—Triacetin (I) (0.1 mol.), ROH (50 c.c.), and *N*-ROH-KOH (6 c.c.) heated at 100° (bath) for 8 hr. give ROAc = decomp. of 48.3, 43.2, and 37.6% of (I) when R = Me, Et, and Pr^o, respectively. Similarly (I) (0.2 mol.) with 0.5*N*-EtOH-KOH (10 c.c.) gives EtOAc and diacetin = 42.6% decomp. of (I), the ester of the sec.-OH underdoing preferential hydrolysis in slightly alkaline medium. J. W. B.

Velocity of bromination of ethyl acetoacetate. II. General basic catalysis. K. J. PEDERSEN (J. Physical Chem., 1934, 38, 601—621; cf. A., 1933, 910).—The velocity of bromination is determined by the consecutive enolisations of Et acetoacetate and the α -Br-ester, which reactions are catalysed by bases. Catalytic consts. of the "bases" AcO', CH₂Cl·CO₂', OH·CH₂·CO₂', H₂PO₄', SO₄'', and H₂O have been determined. Velocities of enolisation are considered to be determined by those of dissociation of the keto-forms. F. L. U.

Velocity of hydration of acetic anhydride. O. FELSENFELD (Chem. Listy, 1934, 28, 89—93).—The velocity coeff. *k* of the reaction Ac₂O + H₂O \rightleftharpoons 2AcOH does not vary with the initial concn. at 10—35° between 0.01 and 0.115*N*; at higher concns. *k* diminishes to a greater extent at higher than at lower temp. At a given concn. *k*₁₀ : *k*₂₀ : *k*₂₅ : *k*₃₀ are as 2² : 3² : 4² : 5². Various acids in concns. >0.1*N* accelerate the reaction, in the order H₂SO₄ > HNO₃ > HBr > HCl, whilst NaOH and KOH retard reaction. The val. of *k* varies in presence of the nitrates, sulphates, chlorides, and bromides of K, Na, Li, and Mg (with the exception of MgSO₄ and LiBr) in accordance with the Grube-Schmid rule (A., 1926, 474). R. T.

Decomposition of α -nitrocarboxylic acids. K. J. PEDERSEN (J. Physical Chem., 1934, 38, 559—571).—From a study of the velocity of decomp. of NO₂·CH₂·CO₂H and NO₂·CMe₂·CO₂H in acetate buffers and aq. HCl of different concns. it is inferred that the ion ·C(NO₂)·CO₂' decomposes to give ·C·NO₂' and CO₂. The calc. dissociation consts. of the two acids are 0.0208 and 0.0118, respectively, at 17.84°. A mechanism for the decomp. of α -nitro- and β -keto-carboxylic acids is suggested. F. L. U.

Velocity of reaction at sulphide surfaces. S. A. KAMENETZKI (J. Appl. Chem. Russ., 1934, 7, 61—72).—The velocity of reaction, *v*, of aq. AgNO₃ with a no. of natural cryst. sulphides \propto the surface of contact; the amount of Ag₂S deposited per sq. cm.

of surface is const. and characteristic of the given sulphide. The val. of *v* increases in the order chalcopryrite > coveline > pyrites > Zn blende > orpiment > galena > chalcosine; this order is identical with that of solubility. R. T.

Influence of oxygen, sulphur dioxide, and moisture on the homogeneous combination of hydrogen with sulphur. E. E. AYNLEY and P. L. ROBINSON (Nature, 1934, 133, 723—724; A., 1933, 911).—In the reaction between S and H₂ containing 0.06 to 7 vol.-% O₂, between 290° and 343° all the O₂ goes to SO₂ in the first few min., after which H₂ reacts with the remaining S at the velocity expected for H₂ alone. Contrary to Norrish and Rideal (J.C.S., 1923, 123, 1689), neither free O₂ nor SO₂ affects the velocity of the H₂-S reaction. In packed bulbs some SO₂ and H₂S react according to the scheme 2H₂S + SO₂ = 2H₂O + 3S, but only at the glass surface; in unpacked bulbs the reaction is undetectable. H₂O has no effect on the H₂-S reaction. L. S. T.

Velocity of reaction between iron and cupric sulphate. S. A. VOZNESENSKI and I. T. NAGATKIN (J. Appl. Chem. Russ., 1934, 7, 51—60).—The process of extraction of Cu from H₂O by Fe ceases when the Fe becomes covered with a uniform layer of Cu; the layer is less adherent with low than with high [Cu]. The velocity of reaction with steel is > with Fe, and is at a max. at 50°; Cl' greatly accelerates reaction. Traces of Cu cannot be removed by passing the H₂O through a column filled with Fe wire; the best procedure is to leave the H₂O in a tank with Fe. R. T.

Passivity of magnesium in chromic acid.—See B., 1934, 542.

Inert gas effect in the radiochemical polymerisation of acetylene. W. MUND (J. Physical Chem., 1934, 38, 635—637).—The catalytic efficiency of CO₂ calc. according to a theory previously developed (A., 1931, 1139) agrees with recently published experimental data (A., 1933, 238). F. L. U.

Efficiency of argon as a radiochemical catalyst. C. ROSENBLUM (J. Physical Chem., 1934, 38, 683—688; cf. A., 1933, 238).—By correcting for the proper efficiency of an ionic catalyst the "depletion" effect is eliminated. About 40% of the ionisation produced in A is utilised in promoting oxidation of H₂ and of CO, and about 60% in the polymerisation of C₂H₂. Corrections of this kind lead to satisfactory velocity coeffs. and vals. of the ratio (no. of mols. per ion-pair) in regions where most of the total ionisation is carried by the A. F. L. U.

Effect of nitrogen peroxide on the kinetics of ethane oxidation. A. I. SERBINOV and M. B. NEIMAN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 297—300).—The velocity of oxidation of C₂H₆ at about 100 mm. and at temp. < 500° is increased by addition of traces of NO₂, the auto-catalytic character of the oxidation ceasing. The following reaction mechanism is suggested: NO₂* + O₂ = NO₂ + O₂*; O₂* + O₂ = 2O₂; O₂* + C₂H₆ = C₂H₆O₂. J. W. S.

Thermal decomposition of acetaldehyde under the influence of various catalysts. H. FROMHERZ (Z. physikal. Chem., 1934, B, 25, 301—318).—The

homogeneous decomp. is catalysed by Br, HCl, and H₂S, the velocity being proportional to the catalyst concn. Temp. coeffs. have been determined. NH₃, C₅H₅N, C₂N₂, HCN, and SO₂ have no catalytic action. Substances which react at low temp. with MeCHO are catalytically inactive; the substances which are catalysts have a high polarisability. The MeCHO, but not the catalyst, has more or less of a deactivating effect on the intermediate compound which determines the reaction, an active complex of MeCHO and catalyst.

R. C.

Protolytic reactions and prototropic isomerisation. K. J. PEDERSEN (J. Physical Chem., 1934, 38, 581—600).—A theory of prototropic reactions similar to that proposed by Ingold, Shoppee, and Thorpe (A., 1926, 939) is discussed. Experiments on the decomp. of NH₂·NO₂ afford strong support for Brønsted's theory of acid and basic catalysis.

F. L. U.

Enzyme catalysis of the ionisation of hydrogen. B. CAVANAGH, J. HORIUTI, and M. POLANYI (Nature, 1934, 133, 797; cf. this vol., 37).—*B. coli* and *B. acidi lactici* (I) catalyse the reaction $\text{HH}^2 + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{HH}^2\text{O}$. For (I) *k* is 0.0065 at 37°.

L. S. T.

Active spots of catalysts. A. FROST and M. SCHAPIRO (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 243—248).—A discussion. Active spots are identified with defects in the crystal lattice (cf. Smekal, A., 1929, 1370).

H. J. E.

Yield of the reaction of synthesis of ammonia at high pressures. L. KOWALCZYK (Przemysł Chem., 1934, 18, 69—84).—A thermodynamical consideration of the reaction leads to the conclusions that the yield of NH₃ in the reaction $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ should increase with pressure, and that an excess of one of the substrates should adversely affect the yield.

R. T.

Catalytic decomposition of lead tetraphenyl. M. KOTON (J. Amer. Chem. Soc., 1934, 56, 1118—1119).—The decomp. of PbPh₄ is catalysed by Pb.

E. S. H.

Activity and crystal structure of mixed metal catalysts. J. H. LONG, J. C. W. FRAZER, and E. OTT (J. Amer. Chem. Soc., 1934, 56, 1101—1106).—Four series of mixed catalysts (Ni-Fe, Ni-Co, Ni-Cu, and Fe-Co) were prepared by reduction of the hydroxides; their crystal structure was determined by the X-ray method and their catalytic activity by the hydrogenation of C₆H₆ to cyclohexane. A substitutional type of solid solution is formed. The activity is related to the arrangement of the atoms in the mixed catalyst.

E. H. S.

Physico-chemical study of the iron catalyst used in the synthesis of liquid hydrocarbons. J. ANTHEAUME, E. DECARRIÈRE, and R. RÉANT (Chim. et Ind., 1934, 31, Spec. No., 421—423).—The catalyst used for the oxidation of CO to liquid hydrocarbons consists of a mixture of oxides of Fe and Cu with K₂CO₃; to be effective it must contain both Fe₂O₃ and Fe₃O₄. The activity is the greater the finer is the crystal structure.

H. S. P.

Catalytic preparation of aniline and its homologues from tar phenols and ammonia.—See B., 1934, 491.

Neutral salt action in the hydrolysis of wool by acids and bases. E. KIMMEL (Bul. Soc. Chim. România, 1934, 15, 121—127).—NaCl favours hydrolysis of wool by 1% HCl, but Na₂SO₄ hinders hydrolysis by 1% H₂SO₄. Na₂SO₄ and Na₂CO₃ hinder to equal extents the action of 0.4*N*- and 0.1*N*-NaOH, the temp. effect being negligible, but in 0.00125*N*-NaOH addition of Na₂SO₄ produces a max. rate of hydrolysis when the salt concn. is about 10%.

H. F. G.

Production of large quantities of heavy water. L. TRONSTAD (Nature, 1934, 133, 872).—The efficiency of separation is only slightly affected by conditions of electrolysis.

L. S. T.

Electrolytic separation of isotopes. R. P. BELL (J. Chem. Physics, 1934, 2, 164—166).—Gurney's treatment of overvoltage (cf. A., 1932, 25), applied to the relative rates of discharge of two isotopes, gives a separation efficiency independent of, or varying only slightly with, the electrode material and c.d. A rough estimate of the possibility of separating Li⁶ and Li⁷ by electrolysis is given.

N. M. B.

Mechanism of electrodeposition. L. B. HUNT (Trans. Electrochem. Soc., 1934, 65, 95—105; cf. B., 1932, 644).—As an alternative to Volmer's "migration" theory of lattice development (cf. A., 1932, 688), which is criticised, it is suggested that metal ions accumulate by adsorption in the double layer until a continuous lattice can be formed therefrom over the face of any particular crystal. The movement of electrons through the cathode surface is dependent on the presence of adsorbed ions in a condition permitting their acceptance of electrons. The lateral spreading observed by Volmer is interpreted as a wave-like succession of electron transitions passing through the adsorbed layer and incorporating it into the lattice.

H. J. T. E.

Electrodeposition of indium from cyanide solutions. D. GRAY (Trans. Electrochem. Soc., 1934, 65, 283—286).—The tendency for In(OH)₃ to ppt. from its solution in excess of aq. NaCN is counteracted by addition of 0.5 g. of glucose per g. of In. The resulting solution keeps indefinitely and can be boiled without decomp.; electrolysis of such a solution containing 30—60 g. of In per litre at 15—40° using insol. anodes yields white, coherent deposits of In at 1—16 amp. per sq. dm.

H. J. T. E.

Electric phenomenon at the surface of the photographic dry plate. T. KINBARA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 275—282).—When a pole of Pt, Pd, Au, Ag, Al, Ni, Cu, Zn, Mg, Cd, Bi, Sb, Pb, or C was kept in contact with the centre of a dry plate laid on sheet metal, and a const. field of 500 volts was applied between the pole and the sheet for about a day, the plate, on developing, showed a characteristic figure consisting of a nucleus and halo, and, in the case of an Fe or Sn pole, a corona. An alternating field gave no figure.

N. M. B.

Preparation of calcium silicite by electrolysis of molten [silicate] bath. M. DODERO (Compt. rend., 1934, 198, 1593—1594; cf. this vol., 372).—Electrolysis of a molten CaSiO_3 bath ($\text{SiO}_2 + \text{CaCO}_3 + 2\text{CaF}_2 + 1/3\text{CaCl}_2$) at 25 amp. per sq. cm. gave cathodic mixtures of CaSi_2 (I) and Si in proportions depending on the temp. (I) was practically the sole product at the m.p. of the bath, 1000° . Yield about 2.5 g. per hr. B. W. B.

Nickel-plating of aluminium.—See B., 1934, 504.

Oxidation-reduction processes at the surface of an interposed membrane during electrolysis of a cupric solution. (MME.) L. GUASTALLA (Compt. rend., 1934, 198, 1679—1680).—A pig's bladder membrane (I), 0.15 mm. thick, was interposed in a cell containing 0.002M-CuCl₂, passing 5 milliamp. per sq. cm. $\text{CuCl}_2 \cdot 3\text{CuO} \cdot 3\text{H}_2\text{O}$, and later CuO , Cu_2O , and Cu, were formed on the anode-chamber (II) surface of (I), and Cu_2O , Cu, and O_2 on the cathode chamber (III) surface, whilst p_{H} increased in (II) and decreased in (III). A section through (I) showed that pptn. was confined to within < 0.03 mm. of either surface. B. W. B.

Electro-crystallisation of metals. IV. Structure of aluminium deposited in the electrolysis of the fused salts AlCl_3 and NaCl. K. M. GORBUNOVA and Z. A. ADSHEMJAN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 564—570; cf. A., 1933, 767).—The optimum concn. of electrolyte for the electrolytic deposition of Al is an equimol. mixture of AlCl_3 and NaCl. The lower is the c.d. the finer are the crystals and the less is the tendency to form dendrites. Pre-treatment of the cathode by anodic dissolution facilitates the formation of a solid deposit, but the latter is generally readily detachable from the cathode as a fine powder. The lower is the temp. the more compact is the deposit. X-Ray measurements show the absence of characteristic orientation in the growth of the crystals, the magnitude of which is always 10^{-2} — 11^{-3} mm. J. W. S.

Electrolytic oxidation of β -hydroxypropionic acid. E. TOMMILA (Suomen Kem., 1934, 7, 87—90b).—Electrolytic oxidation of $M\text{-OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (I) in 5N-NaOH affords at the anode O_2 , CO_2 , CO, H_2 , $\text{H}_2\text{C}_2\text{O}_4$ (II), HCO_2H , and $\text{CH}_2(\text{CO}_2\text{H})_2$, a (?) hydroxyketo-acid giving a green colour with naphthoresorcinol being obtained when a Pt anode is used. Contrary to Miller *et al.* (A., 1894, i, 228), very little resinification occurs when a neutral solution of the pure Na or K salt of (I) is electrolysed, the anodic products being as above [except H_2 and (II)] and, in addition, C_2H_2 , C_2H_4 , C_2H_6 , AcOH, and MeCHO. The amounts of these products obtained with different electrodes (Pt, Ni, Fe), c.d., time, and temp. (0° and 25°) are tabulated and the mechanism of their formation is fully discussed. Anode potential (ϵ_a)—c.d., and ϵ_a —time curves are plotted. J. W. B.

Oxidation of selenium in the glow discharge. E. N. KRAMER and V. W. MELOCHE (J. Amer. Chem. Soc., 1934, 56, 1081—1083).—By the action of O_2 on Se in the region of the negative glow of the discharge

tube, a white deposit, consisting of SeO_2 with γ 57% of SeO_3 , is formed. The product is stable at room temp. and dissolves in H_2O , giving a solution of H_2SeO_3 and H_2SeO_4 . E. S. H.

Heterogeneous chemical reactions in the silent electric discharge. VIII, IX. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1934, 9, 165—174, 175—181).— Cu^{II} , Zr, Ti^{IV} , UO_2 , Fe^{III} , and Cr^{III} nitrates in H_2 yielded NH_4 salts, the hydroxide of the metal, N oxides, and, in some cases, metal and nitrite. Ca and Na sulphites gave hydroxide and H_2S . CdBr_2 , $\text{Hg}(\text{CN})_2$, and AgCN were reduced to metal and the corresponding acid. KCN was unattacked, whilst KClO_4 gave KCl and H_2O . $\text{Hg}(\text{CNS})_2$, NaCNS, and $\text{Pb}(\text{CNS})_2$ gave sulphide, H_2S , and HCN. With $\text{Hg}(\text{CNS})_2$, Hg and HCNS were also produced. D. R. D.

Absorption of light by hydrogen peroxide in alkaline solution. G. BREDIG, H. L. LEHMANN, and W. KUHN (Z. anorg. Chem., 1934, 218, 16—20).—By the progressive addition of NaOH to aq. H_2O_2 the absorption curves are strongly displaced towards longer wave-lengths. The curve for $\text{NaOH} : \text{H}_2\text{O}_2 = 2 : 1$ relates to HO_2' , and the marked difference between the absorption of H_2O_2 and that of HO_2' indicates that the ionisation is accompanied by a change in the mode of interat. linking. F. L. U.

Kinetics of photochemical decomposition of ammonia. Occurrence of an intermediate product NH_4 . L. FARKAS and P. HARTECK (Z. physikal. Chem., 1934, B, 25, 257—272; cf. this vol., 374).—The stationary [H] established on irradiation of NH_3 under various conditions has been determined by means of the reaction $\text{H} + \text{H}_3^{\text{sam}} \rightleftharpoons \text{H} + \text{H}_2^{\text{ortho}}$. The effect of temp. on [H] indicates that the H atoms formed by light absorption are used up in reactions with insignificant heat of activation. [H] is largely independent of the total pressure at 250—760 mm., but falls below 250 mm., is proportional to $I_{\text{abs}}^{0.69}$, where I_{abs} is the light intensity, and passes through a max. with increasing NH_3 pressure. In explanation it is suggested that the H atoms formed by $\text{NH}_3 + h\nu = \text{NH}_2 + \text{H}$ form NH_4 by addition and an equilibrium $\text{NH}_3 + \text{H} \rightleftharpoons \text{NH}_4$ is set up, which at room temp. is almost entirely over to the right, but at 300° has moved to the left. At small NH_3 pressures the establishment of equilibrium is prevented by diffusion of H atoms to the wall. The quantum yield of $\frac{1}{2}$ is explained by the alternative reactions $\text{NH}_4 + \text{NH}_2 = 2\text{NH}_3$ or $=\text{NH}_2 + \text{NH} + \text{H}_2$, the first of which is three times as probable as the second. The rise of the quantum yield above 400° may be due to the above equilibrium moving so far to the left that not sufficient NH_4 remains to react with the NH_2 in this way. R. C.

Photochemical action of complex light. II. C. WINTHER (Z. wiss. Phot., 1934, 33, 52—56).—The val. 9.0% for the transparency of a saturated NiSO_4 solution, as found by Padoa and Vita (this vol., 155), is incorrect, since the spherical aberration of the flask used as a lens was not considered. New, corr. measurements, using a flask of diameter 8.5 cm.,

give an average transparency of 74%. The author's previous criticisms are sustained. J. L.

Sensitivity of photographic films to X-rays at low temperatures. G. E. M. JAUNCEY and H. W. RICHARDSON (*J. Opt. Soc. Amer.*, 1934, 24, 125—126).—Measurements at 103°, 203°, and 295° abs. show that at const. temp. the density of a film \propto the time of exposure to X-rays provided the density is not too high, and that the slope of the density-time curves is a linear function of the temp. if this is not too low. The slopes at 295°, 203° and 103° abs. \propto 1, 0.452, and 0.388. A. G.

Formation of chlorine heptoxide on illumination of mixtures of chlorine and ozone. A. C. BYRNS and G. K. ROLLEFSON (*J. Amer. Chem. Soc.*, 1934, 56, 1250—1251).—The amount of Cl₂O₇ produced \propto the initial O₃ pressure and increases with increasing Cl₂ pressure, but is only slightly dependent on temp. between 20° and 30°. E. S. H.

Photochemical decomposition of phosgene. C. W. MONTGOMERY and G. K. ROLLEFSON (*J. Amer. Chem. Soc.*, 1934, 56, 1089—1092).—On the basis of kinetic measurements a mechanism is put forward from which is derived the rate law $-d[\text{COCl}_2]/dt = kI_{\text{abs.}} - k'I_{\text{abs.}}^2[\text{CO}]^2[\text{Cl}_2]$, which is in accordance with the experimental facts. E. S. H.

Photochemical decomposition of keten. W. F. ROSS and G. B. KISTIAKOWSKY (*J. Amer. Chem. Soc.*, 1934, 56, 1112—1115).—CH₂:CO is decomposed by wave-lengths < 3700 Å., yielding CO and C₂H₄. The quantum yield = 1 approx. at 3130 Å., which with the diffuse structure of the spectrum suggests that CH₂ is formed first. In presence of C₂H₄, CH₂ forms a solid polymeride. E. S. H.

Formation of carbon tetrachloride from chloroform and chlorine in light. H. J. SCHUMACHER and K. WOLFF (*Z. physikal. Chem.*, 1934, B, 25, 161—176).—The rate of reaction in the vapour state at 50—70° is given by $d[\text{CCl}_4]/dt = k[\text{Cl}_2]^2(I_{\text{abs.}})^{\frac{1}{2}}$. The temp. coeff. at 50—60° is 1.45 ± 0.1. O₂ practically suppresses CCl₄ formation and COCl₂ is formed. The reaction has a chain mechanism: Cl₂ + $h\nu$ = 2Cl (1), Cl + CHCl₃ = CCl₃ + HCl (2), CCl₃ + Cl₂ = CCl₄ + Cl (3), CCl₃ + CCl₃ + Cl₂ = 2CCl₄ (4). The energies of activation of (2), (3), and (4) are < 4.3, ~8, and ~0 kg.-cal., respectively. R. C.

Primary process of photochemical decomposition of formaldehyde. I. F. PATAT (*Z. physikal. Chem.*, 1934, B, 25, 208—216).—Investigation of the decomp. of CH₂O vapour under low pressure in presence of O₂ has shown that in decomp. in the continuous region of the absorption spectrum, but not in that in the fine-structure region, H atoms are formed. R. C.

Formation of coloured compounds from primary aromatic amines exposed to the ultra-violet spectrum. H. FREYTAG (*Z. wiss. Phot.*, 1934, 33, 33—38).—Strips of hardened filter-paper, impregnated with aq. or EtOH solutions of the amines, were exposed in a quartz spectrograph. The intensities of colouring at the different wave-lengths were measured, and the results for 18 compounds are

detailed. The amines examined are sensitive only to ultra-violet light, and, for the majority, from 313 m μ to the shorter wave-lengths, the intensity of the reaction varying greatly with λ . J. L.

Photochemistry and absorption spectrum of acetone. R. G. W. NORRISH (*Nature*, 1934, 133, 837).—A criticism (cf. this vol., 582). L. S. T.

Photovoltaic cells containing dye solutions. B. S. V. R. RAO (*J. Physical Chem.*, 1934, 38, 693—701).—Using aq. erythrosin and chrysoidine with Pt electrodes, the max. in the potential-concn. curve is shown to be due to absorption of active radiation by the dye solution. Erythrosin gives rise to negative, chrysoidine to positive, potentials. The e.m.f. \propto (intensity)^{1/2}. The greatest effect is produced by light of λ slightly > that of the principal absorption band of the dye. F. L. U.

Photolysis of diazo-compounds. M. HORIO (*Mem. Coll. Eng. Kyoto*, 1934, 8, 1—7).—Many diazo-compounds are sensitive to light of λ < 4000—4500 Å., and the upper limit agrees with that of mol. absorption. For copying papers of 1-diazo- β -naphthol-4-sulphonic acid and of *p*-diazodiphenylamine sulphate the curve of λ -spectral sensitivity is similar to that of λ -extinction coeff. A. G.

Mutual effect of dyes and fatty acids when exposed to light. M. HORIO (*Mem. Coll. Eng. Kyoto*, 1934, 8, 26—28).—The addition of linoleic acid (I) accelerates the bleaching of eosin (II) and of Victoria-violet (III) by light, and the addition of (II) or of erythrosin accelerates peroxide formation when (I) is exposed to light. A rapid stream of O₂ hinders bleaching of (II) or (III) in the presence of (I). A. G.

Photochemical investigation of plant oils and fatty acids. M. HORIO (*Mem. Coll. Eng. Kyoto*, 1934, 8, 8—25).—When olive oil (I), linseed oil (II), or linoleic acid (III) is exposed to light in presence of O₂ peroxides are formed; in absence of O₂ illumination has no effect. The spectral sensitivity and the extinction curves are parallel. For (II) and (III) λ of the active rays is < 4000 Å. The rate of the photochemical reaction is independent of the time of exposure (1—8 hr.), the supply of O₂ (0.7—7.5 litres per hr.) and the temp. (0.5—25°); it is \propto the concn. of fatty acid (2.5—20%) and to $I^{1/2}$ (1.1—14); a chain mechanism is proposed. For (I) the velocity is a max. at a definite light intensity (I), which is explained by a modification of the chain mechanism. The reaction persists after the exposure is interrupted. A. G.

Dynamics of photosynthesis. W. O. JAMES (*New Phytol.*, 1934, 33, 8—40).—A mathematical interpretation of photosynthesis as a heterogeneous photochemical reaction. A. G. P.

Origin of the β - and γ -ray coloration of alkali baryta, and alkali borate glasses. J. HOFFMANN (*Z. anorg. Chem.*, 1934, 218, 129—138).—Alkali silicate and borate glasses show, under the action of β - and γ -rays, parallel colour changes apparently connected with the constitution of the glasses. A violet colour, probably due to Na₂SiO₃ or Na₂B₂O₄, is obtained with high alkali content.

This changes as acidity increases through grey, due to a labile form of SiO_2 or B_2O_3 adsorbed by the silicate or borate, to yellow or brown due to reduction to Si and B, respectively. It is possible that the similar changes observed in Ba glasses may have a similar origin. M. S. B.

Mechanism of oxidation promoted by ultrasonic radiation. S. LIU and H. WU (J. Amer. Chem. Soc., 1934, 56, 1005—1007).— O_2 mols. at the surface of bubbles are activated by ultrasonic radiation, and have the property of liberating I from KI and reacting with H_2O to give H_2O_2 . CCl_4 and CHCl_3 are oxidised, yielding Cl_2 . E. S. H.

Purity of distilled water. W. L. A. WARNIER (Chem. Weekblad, 1934, 31, 254—255).—The Dutch Pharmacopœia specification for distilled H_2O requires revision, since it permits the presence of sufficient dissolved CO_2 to yield a turbidity with 5% AgNO_3 solution. H. F. G.

Preparation of distilled water. A. A. GUNTZ (Chim. et Ind., 1934, 31, Spec. No., 238—243).—The effect of additions of acid, alkali, and salts, and of conditions of distillation has been studied by measuring the conductivity of fractions of the distillate. H. J. E.

Per-compounds. II. Distinction between different types of per-compounds. F. KRAUSS and C. OETNER (Z. anorg. Chem., 1934, 218, 21—32; cf. A., 1932, 350).—A discussion of methods of distinguishing "true" per-salts from H_2O_2 -additive products. F. L. U.

Reaction of sodium with dry oxygen. B. L. HERRINGTON (J. Physical Chem., 1934, 38, 675—682).—Na amalgams are instantly attacked by O_2 that has been dried with P_2O_5 for more than a year. A surface film of oxide, which protects the metal from further attack, is formed. In presence of H_2O vapour the film is unstable and the Na is slowly but completely oxidised. Oxidation is accompanied by the emission of light. F. L. U.

Preparation of carbonate-free sodium hydroxide. W. STAHL (Z. anal. Chem., 1934, 97, 86—89).—Na reacts with H_2O vapour in a vessel sealed against CO_2 by KOH, warmed to 40° . Explosion may occur if the temp. rises to 50° . J. S. A.

Preparation of pure anhydrous sodium carbonate. W. H. WITHEY (J. Soc. Glass Tech., 1934, 18, 69—70T).—A product free from Fe_2O_3 is obtained by pptn. with EtOH from aq. solution at 50° . The $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ so formed is easily dehydrated without fusion at $> 250^\circ$. J. S. A.

Complexes of mannitol and sorbitol with sodium arsenite and borax. M. SRINIVASAN and M. SREENIVASAYA (J. Physical Chem., 1934, 38, 703—711).—Mixing of mannitol (I) with borax or Na arsenite in aq. solution is accompanied by a considerable increase of vol. Sorbitol behaves similarly. The expansion, as well as the change in optical rotation observed in the case of (I), is regarded as an indication of the formation of compounds. F. L. U.

Phosphorescent beryllium nitride. S. SATOH (Nature, 1934, 133, 837).—The product obtained by

passing NH_3 over a mixture of Be + 10% Al_2O_3 at 1000° shows a blue luminescence after exposure to a Hg-arc lamp. L. S. T.

Complex calcium aluminates. J. FORET (Chim. et Ind., 1934, 31, Spec. No., 722—726).— $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and Ca salts form two series of double salts having the general formulæ $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(A)_2 \cdot 10\text{H}_2\text{O}$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(A)_2 \cdot 30\text{H}_2\text{O}$ (where A is the acid radical). The conditions of pptn. and solubility curves, in the first series for $A = \text{Cl}', \text{Br}', \text{I}', \text{NO}_3',$ and NO_2' and in the second series for $A = \text{SO}_4'', \text{CrO}_4'', \text{SeO}_4'', \text{MnO}_4'', (\text{HCO}_2)'$, have been determined. T. W. P.

Hydrated calcium aluminates. M. ERCULISSE (Chim. et Ind., 1934, 31, Spec. No., 727—731).—A discussion of the system $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ based on results from the system $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. T. W. P.

Reactions in the solid state at high temperatures. XI. Reaction between calcium oxide and silica. W. JANDER and E. HOFFMANN (Z. anorg. Chem., 1934, 218, 211—223).—By heating, at 1000 — 1200° , mixtures of CaO and SiO_2 in different proportions, powdered together for a longer or shorter time, $2\text{CaO} \cdot \text{SiO}_2$ is first formed. For high proportions of CaO (4CaO to SiO_2) and a sufficiently high temp., $3\text{CaO} \cdot \text{SiO}_2$ may next be obtained. In other circumstances the next product is $3\text{CaO} \cdot 2\text{SiO}_2$. As heating continues more SiO_2 , if sufficient is present, enters into combination, and the final product is $\text{CaO} \cdot \text{SiO}_2$. M. S. B.

Action of nitrogen on calcium. H. HARTMANN and H. J. FRÖHLICH (Z. anorg. Chem., 1934, 218, 190—192).—The combination of N_2 with pure Ca, free from alkali and N, ceases as soon as a thin layer of Ca_3N_2 has been formed on the surface. With Ca activated by $< 1\%$ Na, the velocity of N absorption depends on temp. Two modifications of Ca_3N_2 have been obtained, a pseudo-hexagonal form (I) at 300° , a 3.553, c 4.11 Å., d_{calc} 2.72, and a cubic form (II) at 800° , a 11.38 Å., d_{calc} 2.66. (II) is obtained when (I) is heated at 500° (cf. Franck *et al.*, A., 1933, 666). M. S. B.

Calcium oxychloride $3\text{Ca}(\text{OH})_2 \cdot \text{CaCl}_2 \cdot 11\text{H}_2\text{O}$. V. I. NIKOLAEV and S. A. GLINSKICH (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 572—574).—The compound to which the formula $3\text{CaO} \cdot \text{CaCl}_2 \cdot 16\text{H}_2\text{O}$ was attributed by Ditte (Z. anorg. Chem., 1893, 3, 34), Schreinemakers and Figeé (A., 1911, ii, 983) and Milikan (A., 1917, ii, 257) is actually $3\text{Ca}(\text{OH})_2 \cdot \text{CaCl}_2 \cdot 11\text{H}_2\text{O}$, the previous errors being due to the fact that the crystals contain up to 16% of mother-liquor. J. W. S.

New pernitride of strontium and calcium and the imides of the alkaline-earth metals. H. HARTMANN, H. J. FRÖHLICH, and F. EBERT (Z. anorg. Chem., 1934, 218, 181—189).—By heating the alkaline-earth amides $\text{M}(\text{NH}_2)_2$ at approx. 400° , without removing the gases formed, the imides MNH are obtained as yellow, cubic, face-centred crystals. X-Ray data are given. By heating the amides in a high vac. the pernitrides Sr_3N_4 and Ca_3N_4 have been obtained as reddish-brown powders, probably mixed with the corresponding imide.

They dissolve slowly in dil. HCl or H₂O with evolution of NH₃ and N₂. The X-ray spectra contain, besides the imide lines, new lines which cannot be measured owing to a cloudiness which is apparently always found when the pernitride is present. Ba₃N₄ is probably formed similarly. M. S. B.

Precipitation of mercurous hydroxide. W. H. BENNETT (*J. Physical Chem.*, 1934, 38, 573—579).—It is inferred from results of the potentiometric (glass electrode) titration of a dil. HNO₃ solution of Hg₂(NO₃)₂ with NaOH that the ppt. has the approx. composition 3Hg₂O, Hg₂(NO₃)₂.xH₂O. The solubility product of Hg₂(OH)₂ is calc. to be 7.8 × 10⁻²⁴. Hg₂(NO₃)₂ is considerably hydrolysed in HNO₃ at *p*_H between 2 and 3. F. L. U.

Double thiocyanates of mercury and cobalt. II. S. AUGUSTI (*Gazzetta*, 1934, 64, 169—175).—By the action of an aq. solution of KCNS and a Co^{II} salt on a solution of a Hg^I salt (or on solid HgCl) a bluish-green ppt. of Hg₂[Co(SCN)₆] is obtained. This reaction can be used as a qual. test for Hg^I. O. J. W.

Fractionation of actinium in the presence of rare earths. M. CURIE and S. TAKVORIAN (*Compt. rend.*, 1934, 198, 1687—1689).—Fractionation of originally inactive mixtures of La, Nd, and Sm with added Ac, (i) as double NH₄ nitrates and (ii) as double Mg nitrates, gave max. of Ac in different fractions, (ii) being the more effective in concentrating Ac. The activity of fractionated monazite concentrates previously attributed to element 61 is due to Ac (A., 1933, 442). B. W. B.

Combustion of graphite. II. V. SIHVONEN (*Suomen Kem.*, 1934, 7, 83—85B; cf. A., 1933, 1254).—Theoretical. F. L. U.

Preparation of hydrogen compounds of silicon. W. C. JOHNSON and T. R. HOGNESS (*J. Amer. Chem. Soc.*, 1934, 56, 1252).—A mixture of Si hydrides in good yield is obtained by dropping Mg₂Si into a solution of NH₄Br in liquid NH₃. E. S. H.

Nitrosomium chloride. R. SCHWARZ and F. HEINRICH (*Ber.*, 1934, 67, [B], 776—778; cf. Tiede, this vol., 499).—The red compound from NO and HCl is not formed in complete absence of higher oxides of N, although neither N₂O₃ nor NO₂ gives a red compound with HCl. Determination of the m.p. of mixtures of NO and HCl does not disclose a max. at NO.HCl, but the m.p. of HCl is steadily depressed. The other H halides do not appear to react with NO. H. W.

Transformation of phosphorus pentanitride into mononitride. H. MOUREU and P. ROCQUET (*Compt. rend.*, 1934, 198, 1691—1693).—The action of liquid NH₃ on (PNCl₂)₃ gives PN₃H₄ [possibly PN(NH₂)₂; cf. A., 1908, ii, 583] which yields PN₂H at 380°. PN₂H heated in vac. at > 400° gives P₃N₅+NH₃; P₃N₅ decomposes at 700° to PN+N₂, and not to P+N₂ (cf. this vol., 158). PN is volatile at high temp., is decomposed by conc. H₂SO₄, and appears to be dimeric. B. W. B.

Transposition of insoluble phosphates by means of sodium carbonate solution. D. HART, J. COHEN, and J. SIMON (*Rec. trav. chim.*, 1934, 53,

579—583).—The degree of transformation of 24 insol. phosphates by boiling with 1.5*M*-Na₂CO₃ has been determined. The results do not generally agree with calculations from available solubility data. 3*M*-K₂CO₃ is more effective than 1.5*M*-Na₂CO₃. F. L. U.

Preparation of pure arsenic. A. DE PASSILLE (*Compt. rend.*, 1934, 198, 1781—1783; cf. this vol., 377).—Sb was completely eliminated by successive recrystallisation of (NH₄)₂AsO₄, which was then reduced at 1000° in a current of NH₃, and the As finally redistilled in vac. Analysis of As prepared in this way revealed no impurities. B. W. B.

Action of sodium carbonate on niobium pentoxide. P. SÛE (*Compt. rend.*, 1934, 198, 1696—1698).—Study of the rates of evolution of CO₂ from various heated mixtures of Nb₂O₅+Na₂CO₃ indicated the formation of NaNbO₃ at 625° (cf. A., 1932, 1192) and of Na₃NbO₄ (I) at 775°. (I), *d* 3.725, was slightly sol. in H₂O and was decomposed by H₂SO₄ and HCl. B. W. B.

New compounds of bismuth and antimony with iodine and tri(hydroxyethyl)amine. E. JAFFE (*L'Ind. Chimica*, 1934, 9, 618—622; cf. this vol., 396).—The *cryst. compounds*, N(CH₂.CH₂.OH)₃.HI, BiI₃, m.p. 193°, and NH₂.C₂H₄.OH.SbI₃, m.p. 174°, are described. T. H. P.

Binary system sulphur dioxide-water. Two modifications of solid SO₂. E. TERRES and G. RÜHL (*Angew. Chem.*, 1934, 47, 331—332).—A metastable *modification* (β-SO₂, m.p. 62.5°) is first to crystallise from the liquid in presence of traces of H₂O. D. R. D.

Existence of lead and zinc complexes with sulphurous acids. E. TERRES and G. RÜHL (*Angew. Chem.*, 1934, 47, 332—334).—The mutual solubilities of SO₂ and H₂O are not greatly altered in presence of FeO, PbO, ZnO, or CuO even in the crit. regions. Complex Pb-Zn minerals may be extracted with conc. aq. SO₂ under increased pressure and temp. to recover the metals as simple salts. D. R. D.

Decomposition of dithionic acid. H. STAMM and R. ADOLF (*Ber.*, 1934, 67, [B], 726—730).—The hypothesis that the decomp. of H₂S₂O₆ is connected with its transformation into the ψ form is supported by the observation that decomp. occurs at much greater dilution in MeOH or EtOH than in H₂O. Attempts to prepare Me₂S₂O₆ from Ag₂S₂O₆ and MeI led to evolution of SO₂ and production of MeHSO₄ or Me₂SO₄. N₂H₄.H₂S₂O₆ is unexpectedly stable and its behaviour throws little light on the effect of the addition of H⁺ to S₂O₆²⁻. Solutions of KHS₂O₆, NaHS₂O₆, and LiHS₂O₆ can be conc. without decomp. until crystallisation commences but the normal salts separate. A hyd. K₂S₂O₆ and Na₂S₂O₆ lose SO₂ at about 260° and (NH₄)₂S₂O₆ at 242°; the ψ-salt, Ag₂S₂O₆, decomposes at 80—100°, but is stabilised by NH₃. H. W.

Action of sulphur dioxide on solutions of molybdc anions. R. LAUTTÉ (*Bull. Soc. chim.*, 1934, [v], 1, 105—109).—Saturation of aq. solutions of K₂MoO₄, Na₂MoO₄, and (NH₄)₂MoO₄ with SO₂

gives molybdosulphites, $2\text{SO}_2 \cdot 5\text{MoO}_3 \cdot 2\text{M}_2\text{O} \cdot n\text{H}_2\text{O}$, where $n=5, 6$, and 4 , respectively (cf. Rosenheim, A., 1897, ii, 497), which form small transparent crystals, slowly turning blue in the air with evolution of SO_2 . Solutions of molybdosulphites slowly lose SO_2 , especially on heating, this being more pronounced in presence of H_2SO_4 or HCl . SO_2 reduces alkali molybdates in presence of a little H_2SO_4 or HCl , giving a blue solution, which on extraction with BuOH and evaporation of the latter at $80-85^\circ$ yields $\text{Mo}_5\text{O}_{15} \cdot 6\text{H}_2\text{O}$. J. W. S.

Ammonium selenites. J. JANICKIS (Z. anorg. Chem., 1934, 217, 89-103; cf. A., 1932, 584).—The following cryst. salts have been prepared and analysed: $(\text{NH}_4)_2\text{SeO}_3$; $(\text{NH}_4)_2\text{SeO}_3 \cdot \text{H}_2\text{O}$; $(\text{NH}_4)_2\text{Se}_2\text{O}_5$; $(\text{NH}_4)_2\text{Se}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$; $\text{NH}_4\text{H}_3(\text{SeO}_3)_2$. Neither NH_4HSeO_3 nor a sesquiselenite, the existence of which has been reported, could be obtained. Solubility curves for the normal selenite and pyroselenite have been determined. F. L. U.

Formation of perchromates in solution. (MME.) P. RUMPF (Compt. rend., 1934, 198, 1694-1696).— H_2O_2 was added to acid aq. $\text{K}_2\text{Cr}_2\text{O}_7$ or $(\text{NH}_4)_2\text{CrO}_4$, the linear decay of the blue perchromate (I) followed photometrically, and extrapolated to zero time. Max. concn. of (I) always occurred at $\text{CrO}_3/\text{H}_2\text{O}_2=0.5$, supporting the peranhydride CrO_5 suggested by Schwartz and Giese (A., 1932, 708). In solutions of $p_{\text{H}} > 4$ a brown colour formed slowly and was also due to CrO_5 . Equilibrium consts. were determined for acid and alkaline solutions, respectively. B. W. B.

Compounds of uranyl oxalate with alkaline-earth oxalates.—See this vol., 756.

Halogen bleaching liquor reactions. A. SKRABAL (Z. Elektrochem., 1934, 40, 232-246).—Theoretical. On the basis of the known reactions of HOX ($\text{X}=\text{halogen}$) under different conditions, a complete scheme of the steps involved is worked out. E. S. H.

Mixed perchloric and sulphuric acids. I. Simultaneous oxidising and reducing properties of hot concentrated perchloric acid. G. F. SMITH (Ind. Eng. Chem. [Anal.], 1934, 6, 229-230).—The oxidising properties are believed to be due to the decomp. $4\text{HClO}_4 \rightarrow 2\text{Cl}_2 + 7\text{O}_2 + 2\text{H}_2\text{O}$, whilst the reducing properties are assumed to be due to H_2O_2 formed by the reaction $2\text{HClO}_4 \rightarrow \text{Cl}_2 + 3\text{O}_2 + \text{H}_2\text{O}_2$. E. S. H.

Iron complexes. I. Electrical conductivity of the system $n\text{FeCl}_3 \cdot m\text{H}_3\text{PO}_4 \cdot [x\text{H}_2\text{O}]$. B. RICCA and P. MEDURI (Gazzetta, 1934, 64, 235-242).—The data indicate the presence of the acid $\text{H}_3[\text{FeCl}_3(\text{PO}_4)]$ (insol. Ag salt). D. R. D.

Introduction of the azide group into complex salts of cobalt. W. STRECKER and H. OXENIUS (Z. anorg. Chem., 1934, 218, 151-160).—The following complex azides and azido-compounds of Co^{III} have been prepared: $[\text{Co}(\text{NH}_3)_5(\text{N}_3)]\text{N}_3$, sol. in cold H_2O and solution decomposed on heating, decomposed by acids; $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{N}_3)_2$, rather less stable; $[\text{Co}(\text{NH}_3)_4(\text{N}_3)_2]\text{N}_3$, formed first as a reddish-brown violeo- or cis-salt, slightly sol. only in cold H_2O , but dissolving in hot H_2O with decomp., a green praseo- or trans-salt formed on keeping; cis- $[\text{Co}(\text{NH}_3)_4(\text{N}_3)_2]\text{SO}_4$, red, slightly sol. in cold H_2O ; trans- $[\text{Co} \text{ en}_2(\text{N}_3)_2]\text{N}_3$, dark green, red cis-salt formed in solution on heating with H_2O ; $[\text{Co} \text{ en}_2\text{Cl}_2]\text{N}_3$, light green, slightly sol. in H_2O ; cis- $[\text{Co} \text{ en}_2(\text{N}_3)_2]\text{N}_3$, red, easily sol. in H_2O ; $[\text{Co}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}]\text{N}_3$, dark green, insol. in H_2O ; azido-amminocobaltic chlorate, $\text{Co}_2(\text{NH}_3)_6(\text{N}_3)_4\text{ClO}_3$, for which a suitable co-ordination formula has not been found, green, slightly sol. in cold H_2O and decomposed on boiling. All the compounds are more or less explosive. M. S. B.

Physico-chemical methods for the detection of chemical intermediate products. H. SCHMID (Z. Elektrochem., 1934, 40, 274-278).—A review. E. S. H.

"Fundamental error" in mechanical analysis according to Odén's principle. M. VENDEL and E. SZÁDECZKY-KARDOS (Kolloid-Z., 1934, 67, 229-233).—A discussion of the errors in sedimentation analysis. E. S. H.

Analysis of gases. P. WALTER (Chim. et Ind., 1934, 31, Spec. No., 210-212).—The gas is passed through a vertical column in which the absorbent is atomised. The used absorbent is collected and the change in its concn. measured conductometrically. The apparatus is suitable for continuous determination of several gases, a no. of absorbing units being arranged in series. Absorbents for H_2S , SO_2 , NH_3 , CO_2 , O_2 , C_2H_2 , CO , NO , Cl_2 , Br_2 , and S_2Cl_2 are described. H. J. E.

Microanalysis of gaseous mixtures by pressure-temperature curves. J. J. S. SEBASTIAN and H. C. HOWARD (Ind. Eng. Chem. [Anal.], 1934, 6, 172-177).—Apparatus and procedure are based on Campbell's method (Proc. Physical Soc., 1921, 33, 287), in which < 1 ml. of the sample is required. The method is suitable for the analysis of synthetic mixtures of pure hydrocarbons, commercial gas, and gaseous products obtained by the thermal decomp. of coal. The procedure is especially simple when two components form a heterogeneous condensed phase. E. S. H.

New method of gravimetric analysis. (MLLE.) S. CHATELET (Chim. et Ind., 1934, 31, Spec. No., 199).—Pptn. is carried out in a 100-c.c. pycnometer, the vol. is made up to 100 c.c. with H_2O , and the wt. of the ppt. is calc. from its d and that of the supernatant liquid. The method has been tested for the pptn. of AgCl , BaSO_4 , PbSO_4 , and PbCrO_4 . H. J. E.

Capillary analysis. R. DUBRISAY (Compt. rend., 1934, 198, 1605-1607; cf. A., 1918, ii, 368).—The rate of drop formation of 0.5% sapamine (cf. B., 1928, 199) solution in C_6H_6 gave sharp end-points in the titration of 0.01N-HCl with aq. NH_3 and piperazine. B. W. B.

Analytical method for converting the p_{H} into the hydrogen-ion concentration of a solution. M. DÉRIBÉRE (Ann. Chim. Analyt., 1934, [ü], 16, 193-197).—Corresponding vals. of p_{H} and c_{H} are tabulated. J. G. A. G.

Indicators for oxidimetry; phenanthroline and diphenylamine derivatives. L. P. HAMMETT, G. H. WALDEN, jun., and S. M. EDMONDS (J. Amer. Chem. Soc., 1934, 56, 1092—1094).—The prep. of *nitrophenanthroline* (I), m.p. 202°, is described; the relative oxidation potentials and indicator properties of the (I)-ferrous ion, *p*-nitro-, *p*-amino-, and 2:4-diamino-diphenylamine have been investigated. New potential ranges are covered by some of these indicators. E. S. H.

Photo-electric colorimetry in water analysis. E. NAUMANN and K. NAUMANN (Z. anal. Chem., 1934, 97, 81—86).—Photo-electric colorimetry by Lange's direct deflexion method (A., 1933, 44) is employed for the determination of Fe, Mn, and PhOH. Nephelometric determination of H_2SO_4 as $BaSO_4$, and of Pb as PbS in NH_3 solution, is possible, using gum arabic as stabiliser. J. S. A.

Determination of bromide in presence of large excess of chloride. R. F. NEWTON and E. R. NEWTON (Ind. Eng. Chem. [Anal.], 1934, 6, 213—215).—Br is liberated by adding a moderate excess of aq. Cl_2 , collected in aq. Na_2SO_3 , and titrated potentiometrically after oxidation of excess Na_2SO_3 in the air. The max. error is about 0.2% on a sample containing > 4 mg. Br' and about 0.5% for 0.5—1 mg. Br'. Moderate quantities of I do not interfere. E. S. H.

Mercurimetric determination of iodine using diphenylcarbazone as indicator. J. V. DUBSKÝ and J. TRTÍLEK (Mikrochem., 1934, 115, 95—98; cf. A., 1933, 364).—I' is titrated with 0.1N- $Hg(NO_3)_2$, using diphenylcarbazone to indicate excess of Hg^{++} . A sharper end-point is obtained by filtering from pptd. HgI_2 when titration is nearly complete, and completing the titration on an aliquot portion of filtrate. J. S. A.

Sensitivity of the iodine-starch reaction. I. M. KORENMAN (Mikrochem., 1934, 15, 25—31).—The sensitivity in neutral solution rises with increase in [KI] to a max., [I]= $5 \times 10^{-6}N$, when [KI] \leq 0.1%. [KI] necessary to attain max. sensitivity decreases with increasing [H']. J. S. A.

Determination of iodine. A. ITANO (Ber. Ohara Inst. landw. Forsch., 1933, 6, 53—58).—McClendon's closed combustion method gave better results than those of Fellenberg or of Andrew (B., 1930, 579), although in all cases the presence of org. matter markedly lowered the vals. recorded. A modified method is described in which the I is determined colorimetrically (treatment with H_2SO_4 -nitrite and extraction with CS_2) or volumetrically (liberation of I by Br and titration with $Na_2S_2O_3$). An accuracy of 94—99% is claimed. The min. amount of I determinable by this method is 1×10^{-8} g. A. G. P.

Drop methods of detection and determination of fluorine. I. V. TANANAIEV and G. S. SAVTSCHENKO (J. Appl. Chem. Russ., 1934, 7, 229—232).—5 ml. of solution are made alkaline to phenolphthalein with aq. NaOH, excess of aq. $AgNO_3$ (I) is added, the solution is warmed, and aq. $Ca(NO_3)_2$ is added to the filtrate, which becomes turbid if \leq 0.4 mg.

F is present: $CrO_4^{''}$, $Cr_2O_7^{''}$, $PO_4^{'''}$, $AsO_3^{'''}$, $AsO_4^{'''}$, BO_2' , $SiO_3^{''}$, $CO_3^{''}$, Cl', Br', I', CN' , CNS' , $Fe(CN)_6^{''''}$, $Fe(CN)_6^{''''}$, ClO_3' , IO_3' , NO_2' , NO_3' , S'', $SO_3^{''}$, $SO_4^{''}$, $S_2O_3^{''}$, $C_2O_4^{''}$, and OAc' do not interfere. F' is determined by adding excess of (I) to 5—10 ml. of warm solution, diluting to 100 ml., adding excess of NaCl to an aliquot portion, and titrating the solution at 70—80° with standard $AlCl_3$ (Me-red indicator).

R. T.

Determination of minute quantities of sulphide-sulphur. C. E. LACHELE (Ind. Eng. Chem. [Anal.], 1934, 6, 200—201).—The H_2S , obtained by treatment with acid, is collected as a stain on a paper diaphragm impregnated with $Pb(OAc)_2$. A uniform coating is ensured by using a stream of N_2 to dilute the gas. An accuracy of ± 0.002 mg. is possible for 0.008—0.080 mg. volatile sulphide-S. E. S. H.

Determination of sulphur in sulphides. J. HOMMÉ (Przemysł Chem., 1934, 18, 84—86).—Brunck's method (A., 1905, ii, 762) is modified as follows: 1 g. of substance is mixed intimately with 2 g. of CoO and 3 g. of Na_2CO_3 , the mixture is covered with Na_2CO_3 , and heated at 1000° in O_2 during 25 min. for pyrites, and 40 min. for Zn blende. The melt is extracted repeatedly with 2% Na_2CO_3 , the extract is filtered, and $SO_4^{''}$ is determined as usual in aliquot parts of the filtrate. R. T.

Bromo-iodometric researches. IX. [Selenites, selenates, and selenium.] J. H. VAN DER MEULEN (Chem. Weekblad, 1934, 31, 333—335).— $SeO_3^{''}$ (I) is converted into $SeO_4^{''}$ (II) with KI-HCl in presence of a large excess of starch paste to keep the pptd. Se (III) in solution during titration with $Na_2S_2O_3$. (I) is converted into (II) by NaOBr in presence of $KHCO_3$ and excess of OBr' determined iodometrically. (II) is reduced to (I) with HBr and (III) is converted into (II) by boiling with $KBrO_3$ solution prior to determination. S. C.

Detection of selenium and tellurium in presence of one another. N. S. POLUEKTOV (Mikrochem. 1934, 15, 32—34).—Addition of conc. HI (or KI+HCl) to solutions containing Se ppts. Se+I (dissolved by $Na_2S_2O_3$), forming a red spot. Te forms $TeI_6^{''}$, and does not interfere. $TeO_3^{''}$, but not $SeO_3^{''}$, is reduced by $Sn^{''}$ in alkaline solution to a greyish-black stain of Te. Bi, Ag, and metals with coloured hydroxides interfere. J. S. A.

Macro- and micro-detection of nitrous acid, especially with chrysean. J. V. DUBSKÝ, J. TRTÍLEK, and A. OKÁČ (Mikrochem., 1934, 15, 99—106).—Chrysean (2-aminothiazole-4-thioamide) gives with NO_2' in acid solutions a red coloration or dark red-brown ppt., which can afford a quant. separation from NO_3' . Metals of the H_2S group interfere. Limit of detection 0.25×10^{-6} g. 2-Thiol-4-*p*-aminophenylthioldiazole in presence of HNO_2 gives with α - $C_{10}H_7$ -OH a deep red colour (limit 0.1×10^{-6} g. NO_2'). J. S. A.

Analysis of phosphosilicates. A. LASSIEUR (Ann. Chim. Analyt., 1934, [ii], 16, 197—202).—If after separating $PO_4^{'''}$ from the metals by NH_4 molybdate, the Mo is removed from the filtrate (I) by evaporating with HCl and passing H_2S , a Mo-blue

is formed if Fe is present. This is avoided if excess of aq. NH_3 and $(\text{NH}_4)_2\text{CO}_3$ is added to (I) and the ppt. dissolved in HCl before passing H_2S . The traces of Ca and Mg in the filtrate are pptd. by NH_4 oxalate and phosphate, respectively. If the P_2O_5 is < 10% of the wt. of $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$, the first is almost completely pptd. together with $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$, leaving Ca in solution. J. G. A. G.

Determination of traces of arsenic by Cribier's method. II. Application to complex mixtures, in particular to the normal arsenic in urine. H. GRIFFON and M. BUISSON (J. Pharm. Chim., 1934, [viii], 19, 477—497).—Cribier's method (I) is trustworthy only when the As is in relatively pure solution. For urine or other biological fluids, As can be determined by (I) after liberation as AsH_3 and absorption in KMnO_4 . H. G. R.

Selenium as oxidation-reduction indicator in the volumetric determination of arsenite with potassium bromate. L. SZEBELLÉDY and K. SCHICK (Z. anal. Chem., 1934, 97, 186—191).—Colloidal Se functions as a rapid oxidation-reduction indicator for free halogens. To 35 c.c. of As_2O_3 solution containing 5 g. of NaBr, 25 c.c. of conc. HCl are added and after heating at 55—60° 1 c.c. of $\text{M-H}_2\text{SeO}_3$ is added, and the solution titrated at 55° with 0.1N-KBrO₃. J. S. A.

Micro-determination of boric acid. C. ŞUMULEANU and G. GHIMICESCU (Bul. Soc. Chim. România, 1934, 15, 79—89).—The dry sample (0.03—10 mg. of H_3BO_3) and 10 c.c. of MeOH are placed in a distilling flask and 5 c.c. of conc. H_2SO_4 are added slowly. The distillate is passed into 15 c.c. of saturated $\text{Ba}(\text{OH})_2$ solution. When H_2SO_4 fumes appear the flask is cooled, 5 c.c. of MeOH are added, and the distillation is repeated (3 times). The H_3BO_3 in the neutralised $\text{Ba}(\text{OH})_2$ solution (phenolphthalein) is titrated with 0.04N- $\text{Ba}(\text{OH})_2$. The error is > 1.7%. If wine is to be examined it is neutralised with Na_2CO_3 and the determination is carried out on the ignited residue on evaporation. Jorgensen's titration method, Hebebrand's colorimetric method, and the Rumanian official method give errors of the order of 40—50% when only 1—2 mg. of H_3BO_3 is present, although they are satisfactory with 50—100 mg. H. F. G.

Sensitive reaction for boric acid. A. S. KOMAROVSKI and N. S. POLUEKTOV (Mikrochem., 1934, 14, 317—320).—A 0.005% solution of *p*-nitrobenzene-azochromotropic acid (Chromotrope 2B) (I) forms a very sensitive reagent for H_3BO_3 . A drop of slightly alkaline solution under test is evaporated to dryness on a porcelain dish, and 2 or 3 drops of (I) are added. In presence of B the colour changes from bluish-violet to greenish-blue. This method detects 2 p.p.m. of H_3BO_3 . Presence of oxidising anions causes a rose or yellow ppt., so in such cases a drop of the solution should be heated with solid $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ until H_2SO_4 fumes are evolved before addition of (I). In presence of F the acidified test solution should be warmed with SiO_2 to remove the F as SiF_4 before adding the reagent. The method is particularly suited to the detection of B in minerals. J. W. S.

Determination of carbonic acid by loss in weight. C. MAHR (Z. anal. Chem., 1934, 97, 93—95).—The substance is decomposed with 1 vol. of 70% $\text{HClO}_4 + 2$ vols. of saturated aq. NaClO_4 in an apparatus described, warming to 35° if necessary. In presence of Cl' or CN', $\text{Hg}(\text{ClO}_4)_2$ is added to avoid loss of HCl or HCN. $\text{K}_2\text{Cr}_2\text{O}_7$ may be added to oxidise SO_3'' if present. J. S. A.

Determination of carbon monoxide in air.—See B., 1934, 557.

Determination of potassium in mineral waters and other solutions. V. CRASU and V. MANOLE (Bul. Soc. Chim. România, 1934, 15, 129—136).—The K is separated by the use of $\text{Na}_3[\text{Co}(\text{NO}_2)_2]_6$ solution and determined by a modified platinichloride method. The KCl solution (1—2 c.c.) is treated with H_2PtCl_6 and 96% EtOH is added until the EtOH concn. is 80%; pptn. is complete within a few min. The ppt. is dissolved in H_2O and reduced at the b.p. with HCO_2Na , the pptd. Pt being removed and weighed. The error is usually < 2%. A stable solution of $\text{Na}_3[\text{Co}(\text{NO}_2)_2]_6$ which may be kept indefinitely may be prepared by dissolving 100 g. of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 650 g. of NaNO_2 in 800 c.c. of H_2O at room temp., adding 4 c.c. of glacial AcOH, and keeping for 24 hr. The filtered solution is diluted to 1 litre. H. F. G.

[Determination of potassium.] F. ALTEN and H. WEILAND (Z. Pflanz. Düng., 1934, A, 34, 108—110).—A reply to Tischer (this vol., 620).

A. G. P.

Rapid centrifugal determination of small amounts of sodium. E. R. CALEY, C. T. BROWN, and H. P. PRICE (Ind. Eng. Chem. [Anal.], 1934, 6, 202—205).—Na is pptd. by a solution of $\text{Mg}(\text{OAc})_2$, $\text{UO}_2(\text{OAc})_2$, and AcOH in EtOH. The voluminous ppt. is collected by centrifuging in a capillary tube, and its vol. is determined. K and Li interfere seriously when present in sufficiently high concns. E. S. H.

Determination of sodium in potassium salts.—See B., 1934, 539.

Determination of small quantities of sodium carbonate. Warder's method with improved technique. J. E. S. HAN (Ind. Eng. Chem. [Anal.], 1934, 6, 209).—The solution is filtered after reaching the first end-point and before commencing the second titration. E. S. H.

Determination of sodium thiosulphate by means of potassium dichromate. H. C. S. SNETHLAGE (Rec. trav. chim., 1934, 53, 567—578).—In presence of HCl the accuracy of the determination is influenced by illumination, concn. of acid, and rate of addition of KI. Reproducible results are not obtainable except in very dil. solutions. The above factors are far less important when H_2SO_4 is used, and a mode of procedure has been worked out whereby results accurate to 0.01% may be obtained. F. L. U.

Application of spectrum analysis to determination of alkalis and alkaline earths. II. Micro-determination of sodium and lithium. W. H. JANSEN and J. HEYES. III. Micro-determin-

ation of sodium in native blood serum. W. H. JANSEN, J. HEYES, and C. RICHTER (Z. physikal. Chem., 1934, 168, 257—266, 267—273; cf. A., 1932, 1103).—II. The spectroscopic determination by spraying the solution containing the Na or Li into a flame has been studied. The first step is to ascertain the concn. range over which there is an approx. linear relation between the concn. and the blackening of the photographic plate caused by the light emitted, the unknown concn. then being determined by interpolation. To eliminate errors due to local variations in the emulsion the test solution is photographed between solutions of known concns. Determinations of satisfactory precision can be made with Na and Li concns. down to 0.05 and 0.001 mg. per litre, respectively.

III. In applying the above method to the determination of Na in blood serum the latter is diluted at least 1000 times and sprayed directly into the flame; the high d and η of undiluted serum interfere with the spraying and render the method inapplicable. The results agree with those obtained from a solution of the serum ash. The Na content of the blood serum of a healthy person varies from 300 to 350 mg. per 100 c.c. R. C.

Direct potentiometric determination of heavy-metal ions with potassium cyanide and sodium sulphide. W. HILTNER and W. GRUNDMANN (Z. anorg. Chem., 1934, 218, 1—15; cf. this vol., 48).—Accurate results in the potentiometric titration of Ag and a no. of bivalent metals can be obtained by using a Ag_2S electrode. Ag, Ni, Co, and Cu, Ag in presence of Ni, Cd, Zn, Cu, or Co, Ni in presence of Cd or Zn, and Co in presence of Cd or Zn are determined by titration with KCN. Ag, Cu, Cd, and Zn, Ag in presence of Cu, Cd, Zn, Cu+Cd, or Cu+Zn, and Zn in presence of Mn can be determined with Na_2S . The following pairs are determined by combined titration with KCN and Na_2S : Ni+Cd, Ni+Zn, Co+Cd, Co+Zn. F. L. U.

Identification of silver cyanide and thiocyanate. L. M. KULBERG and J. A. SEMENTZOV (Ukrain. Chem. J., 1933, 8, 168—170).—The Bunsen flame is coloured violet-red by AgCN, and blue by AgCNS; these colorations afford a means of detection of CN' and CNS'. R. T.

Potentiometric determination of heavy-metal ions with sodium sulphide. W. HILTNER and W. GRUNDMANN (Z. physikal. Chem., 1934, 168, 291—307).—Ag, Cu, Cd, and Zn can be determined potentiometrically by titration with 0.1N- Na_2S using a Ag_2S electrode with a valve potentiometer and titrating rapidly to minimise the adsorption error. The determination of Ag, Cu, and Cd, of Ag, Cu, and Pb, and of Ag, Cu, and Zn in presence of each other is also possible. The heavy-metal sulphides are pptd. one after another and do not form solid solutions. The solubility products increase in the order $CuS < PbS < CdS < ZnS$. Although Ag_2S is more sol. than CuS it is pptd. first. Bi, Pb, Ni, Co, Mn, Sb, and As cannot be determined as above owing either to sulphide formation being too slow or adsorption of S' ions too great. R. C.

Drop reaction of beryllium. A. S. KOMAROVSKY and N. S. POLUEKTOV (Mikrochem., 1934, 14, 315—317).—When a HCl solution of 1.38 g. of $p-NH_2 \cdot C_6H_4 \cdot NO_2$, cooled to 0°, is diazotised by addition of an aq. solution of 0.85 g. of KNO_2 , and the product mixed with a NaOH solution of orcinol (1.42 g.) at 0°, a bright red solution is obtained, which on acidifying gives bright red flakes of *p-nitrobenzeneazo-orcinol*, which dissolve in alkali hydroxide with a yellow colour. When a drop of a 0.025% solution of the compound in NaOH is placed on a filter paper, a drop of the solution to be tested for Be added in the centre of this with a capillary tube, and then another drop of reagent applied, Be gives an orange-red and Mg a brownish-yellow colour. Zn gives a similar colour to Be, but the colour disappears on addition of a drop of 25% KCN solution. The latter also removes oxide colours due to Ni, Co, Cu, Cd, and Ag. Ca, Sr, Ba, Al, La, Pr, Nd, Ce, Zr, and Th do not affect the test. The sensitivity is 1 part in 200,000 for Be alone, or 1 part in 66,000 in presence of 750 times the same amount of Zn. J. W. S.

Determination of magnesium with titan-yellow by Kolthoff's method. C. URBACH and R. BABIL (Mikrochem., 1934, 14, 343—361).—Kolthoff's method (A., 1927, 847) is rendered more rapid and accurate by employing comparison with Mg solutions of known concn. J. W. S.

Detection of zinc by an induced precipitation. P. KRUMHOLZ and J. V. SANCHEZ (Mikrochem., 1934, 15, 114—118).—Co-pptn. of $Co[Hg(CNS)]_2$ from solutions containing 0.01% Co with $Zn[Hg(CNS)]_2$ (cf. this vol., 49) occurs immediately with traces of Zn down to a limiting concn. 1 : 500,000. A blue ppt. collects at the interface on shaking with Et_2O . In the absence of Zn, pptn. is delayed. J. S. A.

Determination of small amounts of zinc in steel and iron.—See B., 1934, 542.

Oxidation of thallos to thallic salts, and reduction of the latter by sodium arsenite in analytical chemistry. F. ČUŤA (Chem. Listy, 1934, 28, 37—41, 58—59).— Tl^{II} is oxidised to Tl^{III} by Br in acid solution containing NaCl, in absence of which reduction of Tl^{III} takes place readily on warming. The solution is added to standard alkaline aq. Na_3AsO_3 , excess of which not oxidised by Tl^{III} is determined by titration with 0.1N-I, and the Tl content is hence calc. The mean error is $\pm 0.2\%$. R. T.

Indirect potentiometric determination of copper. G. SPACU and P. SPACU (Z. anal. Chem., 1934, 97, 99—102).—Cu is pptd. as $[Cu(CNS)_2(C_5H_5N)_2]$ by addition of excess of 0.1N-KCNS + C_5H_5N , and the vol. made up to 100 c.c. Excess KCNS in 50 c.c. of the liquid is titrated back potentiometrically with 0.1N- $AgNO_3$. J. S. A.

Potentiometric determination of copper with thiocyanate. W. HILTNER and W. GRUNDMANN (Z. anal. Chem., 1934, 97, 172—179).—Titration is performed at 65—70° in presence of $NaHSO_3$ as reducing agent, using a AgBr or AgI indicator electrode (cf. this vol., 48). Indirect titration is preferable, using glucose or $N_2H_4 \cdot H_2SO_4$ as reducing agent, in

presence of NaOAc. The solution is then acidified with AcOH and excess CNS' titrated back directly with AgNO₃, using a AgI electrode. The pptn. is sp. except in presence of Ag or Hg. J. S. A.

Volumetric determination of copper with iodide+thiocyanate. D. KRÜGER and E. TSCHIRCH (Z. anal. Chem. 1934, 97, 161—171).—The side reactions leading to a progressive decrease in the titre are discussed. For stability, the proportion of KI should be $\leq 8-10\%$ of the KCNS. Standardisation of the Na₂S₂O₃ against Cu solutions under identical conditions is desirable (cf. A., 1930, 444). J. S. A.

Rapid determination of copper. A. TETTMANZI (L'Ind. Chimica, 1934, 9, 609—610).—When halides are absent, the method previously described (Atti Sci. Torino, 1933—1934, 69, 197) may be modified to determine larger amounts of Cu as follows. The neutral or slightly acid solution is treated, in a 250-c.c. flask, with 15% aq. C₅H₅N and a known vol. of 0.1N-KCNS. After 30 min. the liquid is made up to 250 c.c. with H₂O, mixed, and filtered through a dry filter. 200 c.c. of the filtrate are treated with excess of 0.1N-AgNO₃ and a few c.c. of aq. ferric alum, and the liquid is titrated with KCNS. The method is disturbed by salts of Ni, Co, Mn, Zn, or Cd. T. H. P.

Determination of aluminium in nickel alloys.—See B., 1934, 504.

Direct analysis of mixtures of aluminium hydroxides and calcium aluminates. H. LAFUMA (Chim. et Ind., 1934, 31, Spec. No., 234—235).—The sample is treated with 0.1N-HCl, the residual insol. Al₂O₃ and the sol. Al₂O₃ and CaO being determined. These operations are repeated on a further sample ignited for 1 hr. at 600°. Ignition renders free hydrated Al₂O₃ insol., the Ca aluminates remaining sol. The existence of hydrated Al₂O₃.2CaO has been confirmed. At 80° in presence of mother-liquor it forms cubic Al₂O₃.3CaO.6H₂O. H. J. E.

Crum-Volhard reaction as a drop reaction for manganese. M. P. BABKIN (Ukrain. Chem. J., 1933, 8, 179—181).—1 ml. of solution is boiled for 1 min. with excess of NaOH and 2—3 drops of 3% H₂O₂, and the washed ppt. is boiled with PbO₂ and 2—3 ml. of 10% HNO₃ or 2N-H₂SO₄, when a violet coloration is indicative of Mn. Other cations do not interfere. R. T.

Spectral analysis by sensitive lines within the range of the glass spectrograph. Spark spectrum of a selenium-chromium-nickel steel. W. KRAEMER (Z. anal. Chem., 1934, 97, 89—93; cf. this vol., 621).—Results are given for a Cr-Ni steel containing Se, using the apparatus described previously (A., 1932, 355). J. S. A.

Drop reaction for (a) cobalt, (b) zinc. L. M. KULBERG (Ukrain. Chem. J., 1933, 8, 133—139, 190—192).—(a) A drop of solution, containing $\leq 1.85 \times 10^{-3}$ mg. Co, gives a blue spot when placed on filter paper moistened with saturated aq. (NH₄)₂Hg(CNS)₄ (I). The reaction is untrustworthy when the proportion of other metals to Co is : Cu:Co >

50 : 1; Fe > 1500 : 1; Zn > 2000 : 1; Cd or Ag > 1000 : 1.

(b) 3—4 drops of dil. aq. CoSO₄ and 0.5 c.c. of (I) are added to 1 c.c. of the slightly acid solution under examination, when a dark blue ppt. indicates the presence of $\leq 1.5 \times 10^{-5}$ mg. Zn; NH₄, Mg, Ca, Ba, Sr, Al, Mn, Pb, Ag, Hg^{II}, Sn^{IV}, As, Sb, and small quantities of Co, Ni, and Cr do not interfere. In presence of Fe excess of NaF should first be added, in presence of Hg^I excess of NH₄Cl, and in presence of Sn^{II} excess of HgCl₂. R. T.

Indirect potentiometric determination of cobalt. P. SPACU (Z. anal. Chem., 1934, 97, 192—195).—Co(SCN)₂(C₅H₅N)₄ is pptd. by addition of excess of 0.1N-KCNS and 1 c.c. of C₅H₅N, and excess of KCNS in an aliquot portion of the liquid titrated back potentiometrically with AgNO₃. J. S. A.

Separation of nickel and cobalt by means of alkali phosphates. M. H. WUNSCHENDORFF and (MME.) P. VALIER (Bull. Soc. chim., 1934, [v], 1, 85—90).—The NiS and CoS are treated with the min. quantity of aqua regia, and, after complete dissolution, evaporated to dryness. The NiCl₂ and CoCl₂ are taken up in very little H₂O and filtered. To 2 c.c. of this solution are added 1.5 c.c. of 2N-(NH₄)₂CO₃ and then 1.5 c.c. of 2N-(NH₄)₂HPO₄, after which it is brought to the b.p. 20 drops of conc. aq. NH₃ are added, boiling is continued for 4 min., and the liquid is filtered immediately. The presence of Ni is shown by a turquoise-blue filtrate and the presence of Co by a violet-blue ppt. on the filter. Ni and Co can also be separated in a buffer solution of p_H 6.2 (8.06 c.c. M/15 KH₂PO₄ + 1.94 c.c. M/15 Na₂HPO₄) in the cold or of p_H 5.5 (9.55 c.c. M/15 KH₂PO₄ + 0.45 c.c. M/15 Na₂HPO₄) at the b.p. If 2 drops of N-CoCl₂-NiCl₂ solution are added to 10 c.c. of the buffer solution, Co gives a ppt., whilst Ni can be detected by the blue colour produced on adding NH₃ to the filtrate. The separation is not quant. J. W. S.

Microanalysis of uraninite. F. HECHT and H. KRAFFT-EBING (Mikrochem., 1934, 15, 39—54; cf. A., 1933, 366).—A detailed account of procedure, using 30 mg. of material. J. S. A.

Quantitative spectral determination of tin in copper. J. E. R. WINKLER (Z. anorg. Chem., 1934, 218, 45—48).—Homologous pairs of lines are given for 17 bronzes containing 0.02—14% Sn. F. L. U.

Colorimetric determination of titanium in silicates. N. I. BUDAKOV (J. Appl. Chem. Russ., 1934, 7, 233—234).—0.5 g. of substance is fused with 3.5 g. of Na₂CO₃, the melt is treated with 25 ml. of H₂O and 6 ml. of conc. H₂SO₄, 100 ml. of H₂O are added on complete pptn. of SiO₂, the solution is filtered, 3—5 ml. of 3% H₂O₂ are added to the filtrate + washings, and TiO₂ is determined as usual. R. T.

Quantitative separation of antimony and tin. RAYMOND (Compt. rend., 1934, 198, 1609—1611).—A solution of Sn and Sb in HCl is oxidised with Br and excess of NH₄HCO₃ is added. SnO₂ is pptd. by N(C₂H₄.OH)₃ (cf. Jaffe, A., 1933, 246) and washed with 2—3N-HCl, further separation of Sn from the washings being necessary. Sb is determined in the final combined filtrates. B. W. B.

Colorimetric determination of bismuth. II. Absolute colorimetric determination of bismuth using "grey solution." C. MAHR (Z. anal. Chem., 1934, 97, 96—99).—Bi is determined colorimetrically by comparison with the standard "grey solution" in light of 462 μ as its complex with $\text{CS}(\text{NH}_2)_2$ (I), in 5—8% HNO_3 solution saturated with (I) at 18° (cf. A., 1933, 1134). CNS' if present produces a yellow colour with an absorption max. and extinction coeff. close to those produced by (I), and does not interfere. Cl' interferes, as do Cu and Pb in large amount.

J. S. A.

Quantitative spectroscopic analysis of solutions. W. R. BRODE and J. G. STEED (Ind. Eng. Chem. [Anal.], 1934, 6, 157—159).—Calibration curves have been determined for the spectrographic determination of Nb, Be, Ti, V, W, Fe, Mo, Cr, Pb, and Co in solutions of their compounds. The average error in samples of known composition is < 5%.

E. S. H.

Detection and determination of small contents of platinum metals. H. WÖBLING (Ber., 1934, 67, [B], 773—776).—The solution of the chlorides of the Pt metals from which Os, Ru, and Au have been removed is rendered ammoniacal, treated with so much HCl that the solution is approx. N, and then gradually with SnCl_2 until the intensity of the colour does not increase. The solution is shaken with 2 vols. of EtOAc, the aq. and ester layers are washed with EtOAc and SnCl_2 -HCl, respectively, and Pt is determined colorimetrically in the EtOAc. After 1—2 hr. the Rh colour is removed by EtOAc in which Rh is determined colorimetrically. The aq. phase is treated with NH_3 to develop the green reaction of Pd and, after its determination, is treated with excess of Cl_2 - H_2O , allowing Ir to be determined from the intensity of the brown colour. Occasionally the Pd reaction is ill-defined; in such cases Pd is pptd. by contact with KI over-night and determined after dissolution in Cl_2 - H_2O . By means of active C minute amounts of Pt, Pd, Os, and Ru can be adsorbed from 0.1N-HCl to a residual concn. of 10^{-8} g. per litre, or 10^{-7} g. per litre in the case of Rh. Little adsorption occurs with Ir. The metals can be removed from the adsorbates by hot conc. solutions of NaCl or HCl. Higher concns. of acids or small amounts of C render adsorption less complete. The adsorptive power of SiO_2 gel for Pt metals is slight in acid, immediate and marked in ammoniacal, solution. Pt, Ir, Rh, and Ru are completely, Os and Pd incompletely, co-pptd. when Fe^{+++} or Al is pptd. by NH_3 .

H. W.

Liquefaction of helium by an adiabatic method without pre-cooling with liquid hydrogen. P. KAPITZA (Nature, 1934, 133, 708—709).—The apparatus described liquefies He at the rate of 1 litre per hr., 45 min. after the preliminary cooling to the temp. of liquid N.

L. S. T.

Isothermic diphenylmethane calorimeter, and its applications. A. N. SCHTSCHUKAREV, I. P. KRIVOBABKO, and L. A. SCHTSCHUKAREVA (J. Appl. Chem. Russ., 1934, 7, 259—261).—A Bunsen calorimeter containing CH_2Ph_2 in place of H_2O is more convenient for measuring heat evolved in slow reactions.

R. T.

Comparison of gas analysis by fractional combustion with calorimetric measurements. S. MISCHONSKIY (Chim. et Ind., 1934, 31, Spec. No., 258—263).—An apparatus is described. C. W. G.

Improvements in the adiabatic microcalorimeter. W. SWIENTOSŁAWSKI (Rocz. Chem., 1934, 14, 185—188).—A description of apparatus. R. T.

Measurement of dew point of natural gases. A. MICHELS and G. W. NEDERBRACHT (Ind. Eng. Chem. [Anal.], 1934, 6, 165—166).—Apparatus and technique are described. E. S. H.

Apparatus for the determination of the dew point. E. B. MOSS (Proc. Physical Soc., 1934, 46, 450—458).—An optical system, using diffraction by the dew droplets in a mirror, is applied to an automatic photo-electric apparatus for maintaining a mirror at the dew point. N. M. B.

Thermocouples for the measurement of small intensities of radiations. L. HARRIS (Physical Rev., 1934, [ii], 45, 635—640).—The use of a.c. amplification of voltages produced in very thin thermocouples is developed, and gives a sensitivity 100 times that with thermocouple galvanometer arrangements.

N. M. B.

Measurement of temperature of sound fields. E. A. JOHNSON (Physical Rev., 1934, [ii], 45, 641—645).—A thermocouple for measuring alternating temp. in air due to sound waves up to 5000 cycles per sec. is described. N. M. B.

Comparator for p_H determinations. H. C. P. GEERLIGS (Tijds. Alg. Tech. Ver. Beet. Fabr. Raff., 1934, 29, 89—90).—A roulette form of comparator, in which there is a field of vision divided into two parts brought to equal intensity by manipulating a screw, is described. There are 17 cavities to take the standard tubes, each of which in succession can be brought into line with the comparator containing the assay tube to effect comparison. J. P. O.

Photronic colorimeter and its application to the determination of fluoride. L. V. WILCOX (Ind. Eng. Chem. [Anal.], 1934, 6, 167—169).—The instrument uses two photo-electric cells of the type that transforms light energy into electrical energy directly without the use of an external e.m.f. The cells are electrically opposed and the current developed is balanced by a variable resistance. The method may be applied to the determination of small amounts of F' by Armstrong's method (A., 1933, 1132) with an accuracy of ± 0.1 p.p.m. E. S. H.

Colorimetry with a spectrometer. R. A. HOUSTON (Phil. Mag., 1934, [vii], 17, 1047—1057).—An improved instrument by means of which the colour is interpreted graphically in terms of λ on a colour diagram is described. N. M. B.

Colorimetry with the photo-electric tube. I. K. YAMAMOTO and M. ABE (Bull. Waseda Appl. Chem. Soc., 1933, 21, 1—16).—Results of studies with methylene-blue, quinoline-yellow, and eosin-red are described. CH. ABS.

Apparatus for colorimetric examination of traces. A. A. GUNTZ (Chim. et Ind., 1934, 31, Spec. No., 236—237).—A simply constructed color-

meter, with comparison tubes of 2—6 mm. diam., is described. H. J. E.

Autocollimation mirror monochromator and spectroscope of focal aperture 1:4. C. FORCH (*Z. Physik*, 1934, 89, 87—89). A. B. D. C.

Immersion liquids of intermediate refraction (1.450—1.630). R. D. BUTLER (*Amer. Min.*, 1933, 18, 386—401).—A kerosene fraction of high b.p. and $1\text{-C}_{10}\text{H}_7\text{Cl}$ are used. CH. ABS.

Optical properties of ideal solution immersion liquids. M. J. BUERGER (*Amer. Min.*, 1933, 18, 325—334).—Mixtures of two chemically similar liquids have optical properties which are linear functions of composition. The properties and the prep. of a correction chart are discussed. CH. ABS.

Measurement of concentration during photographic recording of chemical reactions. G. FOURETIER (*Compt. rend.*, 1934, 198, 1689—1691).—The apparatus previously described (*A.*, 1932, 486, 491) has been improved and adapted to record reactions occupying up to 18 hr. B. W. B.

Highly reflecting films of zinc sulphide. A. H. PFUND (*J. Opt. Soc. Amer.*, 1934, 24, 99—102; cf. *A.*, 1933, 1226).—Thin films of ZnS showing first-order interference and high reflecting power can be produced by distillation of sphalerite. The use of such films in physical instruments is discussed. R. S.

Zone plate determination of dominant wavelengths of filtered lamp light. J. W. ELLIS and B. W. SORGE (*J. Opt. Soc. Amer.*, 1934, 24, 103—106).—Dominant λ have been determined for a no. of Wratten gelatin filters and compared with the centres of gravity of the appropriate luminosity curves. R. S.

Physical methods in the chemical laboratory. XXI. New applications of dielectric measurements to technical and analytical purposes. L. EBERT (*Angew. Chem.*, 1934, 47, 305—315).—The theory and practice of measuring dielectric const. ϵ are described. ϵ may be used for testing the purity of liquids. A cell for continuous measurement of ϵ of a distillate as it flows from a condenser is illustrated. ϵ may be used as an indicator in sedimentation analysis of powders. Total H_2O , or its partial pressure over hydrates, may be determined by its effect on the ϵ of dioxan. Mechanical measurements, such as variations in thickness of wires, are also detailed. D. R. D.

Determination of dielectric constants by means of radio. M. M. OTTO and H. H. WENZKE (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 187—188).—Results obtained with the apparatus and procedure described are in good agreement with the recognised vals. E. S. H.

Laboratory apparatus for the measurement of dielectric constants. L. EBERT and E. WALDSCHMIDT (*Chem. Fabr.*, 1934, 7, 180—183).—The apparatus measures the square of the electric refractive index (I) for electromagnetic waves of 150 m. length. It is based on the principle that the frequency of a vibrating electromagnetic circuit depends on the sum of all capacities in the circuit. Capacity

is the quantity actually measured, an empty condenser being filled with the liquid to be tested. (I) can be determined if the apparatus can be calibrated with sufficiently pure liquids. C. I.

Electrical indicator for viscosity measurements.—See B., 1934, 507.

Simple arrangement for the measurement of small conductivities ($x \approx 10^{-8}$) of non-aqueous solutions. W. PHILIPPOFF (*Ber.*, 1934, 67, [B], 811—818).—An apparatus for measurement of the conductivity of very dil., non-aq. solutions (mainly glacial AcOH) is described. H. W.

Apparatus for exact determination of conductivity. E. MICHALSKI (*Rocz. Chem.*, 1934, 14, 177—184).— SiO_2 conductivity apparatus which obviates the possibility of contamination by atm. CO_2 , NH_3 , or H_2O , by sol. constituents of the vessels, or by tap-grease, is described. R. T.

Choice of catalysts for the hydrogen electrode. A. E. LORCH (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 164—165).—A discussion of the relative merits of Pt, Pd, and Ir. E. S. H.

Metallised-glass quinhydrone electrodes. E. NEWBERY (*Trans. Electrochem. Soc.*, 1934, 65, 107—113).—Of various metallised glass surfaces (cf. B., 1933, 925) used as quinhydrone electrodes in solutions of various types, bright platinised or Au-coated glass proved as accurate as Pt wire or sheet; it has the advantages of very low cost, less liability to damage during "flaming," lower sensitivity to impurities, and easy renewal of surface. The rate of attainment of equilibrium is about the same for both types of metallised glass electrode. H. J. T. E.

Glass electrode. E. P. LAUG (*J. Amer. Chem. Soc.*, 1934, 56, 1034—1036).—The trustworthiness of the membranes in the MacInnes glass electrode can be checked by means of their H_2 electrode function, asymmetry potential, and d.c. resistance. E. S. H.

Cells with air electrodes. E. BAUR (*Z. Elektrochem.*, 1934, 40, 249—252).—The cells described contain an air electrode consisting of a "cushion" of Ni wire net, filled with C granules, which is immersed partly in the electrolyte (aq. NaOH), the remainder being exposed to the air. An Fe electrode, consisting of Fe shavings in a Ni wire net container, is described. The electromotive behaviour of these electrodes has been examined. E. S. H.

Adsorption electrodes. I. Glass electrode. H. J. C. TENDELOO (*Proc. K. Akad. Wetensch. Amsterdam*, 1934, 37, 212—215).—Certain glass membranes after treatment with CaCl_2 solution, in order to replace the cations in the capillary layers of the glass by Ca, appear to be able to function as Ca electrodes. H. S. P.

Use of the quinhydrone electrode in the determination of the activity of the hydrogen ion in a solution of sucrose that is undergoing catalytic inversion by hydrochloric acid at 25°. W. W. FLOYD (*Trans. Kansas Acad. Sci.*, 1933, 36, 118).—The cell $\text{Ag} (s), \text{AgCl} (s), \text{Cl}^- (0.1M\text{-HCl} + 0.1M\text{-sucrose}) || \text{H}^+ (0.1M\text{-HCl} + 0.1M\text{-sucrose}) + \text{benzoquin-}$

one (s), quinol (s), Au (s) does not give reproducible potentials.

CH. ABS.

Static charge on a galvo-millivoltmeter. H. A. BROMLEY (*Nature*, 1934, 133, 760).—Attention is directed to a possible source of error in p_H determinations owing to a static charge on the glass being responsible for an erratic behaviour in a Unipivot galvo-millivoltmeter.

L. S. T.

Geiger-Müller counters. M. COSYNS and J. DE BRUYN (*Bull. Acad. roy. Belg.*, 1934, [v], 20, 371—394).—A general survey of the construction and factors affecting the working of the instrument.

N. M. B.

Magnetic objective for the electron microscope. E. RUSKA (*Z. Physik*, 1934, 89, 90—128).

A. B. D. C.

Camera for electron diffraction. W. G. BURGERS and J. C. M. BASART (*Physica*, 1934, 1, 543—548).—The apparatus described is adaptable for the transition or reflection method. The specimen may be heated at 500°.

H. J. E.

Tapless micro-burette with liquid cut-off for serial determinations. R. LINKS (*Mikrochem.*, 1934, 15, 87—94).—A precision form, operated by a Hg-immersed screw plunger, is described.

J. S. A.

Calibration [of pipettes]. J. E. HEARN (*Science*, 1934, 79, 458—459).

L. S. T.

Stirrer for solvent extraction. J. A. PATTERSON, jun. (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 171).

E. S. H.

Drier for sensitive materials. E. JANTZEN and H. SCHMALFUSS (*Chem. Fabr.*, 1934, 7, 112).—The vapour of a liquid of suitable b.p. passes through a series of hollow shelves on which the material to be dried is placed. The shelves are covered with a bell-jar connected to a condenser and vac. pump.

H. F. G.

High-temperature vacuum desiccator of Jena glass. E. RUPP (*Chem.-Ztg.*, 1934, 58, 403).—A desiccator composed of Jena Durax vessels (a baking dish and a bell-jar) may be heated with a H₂O-bath, an electric hot plate, or a free flame covered with gauze or asbestos.

A. G.

Growth of large specimens of single-crystal zinc. C. A. CINNAMON (*Rev. Sci. Instr.*, 1934, [ii], 5, 187—190).—Apparatus and technique for growing a strain-free crystal about 1.2 sq. cm. in cross-section and 35 cm. long of any desired orientation are described. An initial gross mosaic structure may be eliminated by a steep temp. gradient. The ratio of the temp. gradient to the rate of growth must be near a certain favourable val. peculiar to each orientation.

N. M. B.

Improved model of the Salvioni spring balance. A. FRIEDRICH (*Mikrochem.*, 1934, 15, 35—38).—A robust micro-balance, based on the deflexion of a steel watch-spring beam, is described.

J. S. A.

Ozoniser for liquid air temperature. A. C. BYRNS (*J. Amer. Chem. Soc.*, 1934, 56, 1088—1089).—

In the apparatus described pure liquid O₃ can be prepared.

E. S. H.

Automatic mercury air pump with electromagnetic pressure gas distributor. P. SAFFERT and W. WUSTROW (*Z. Elektrochem.*, 1934, 40, 231—232).

E. S. H.

Rapid determination of specific gravity. V. F. SHURAVLEV (*J. Appl. Chem. Russ.*, 1934, 7, 263—269).—Apparatus for determining the d of solids is described.

R. T.

Volumetric determination of the density of air adsorbed by powders. M. V. TSCHAPEK (*Kolloid-Z.*, 1934, 67, 145—148).—Apparatus and technique for determining the adsorbed air by displacement with H₂O are described. Results are given for SiO₂, Al₂O₃, Fe₂O₃, C, starch, and clay.

E. S. H.

Laboratory apparatus. P. FUCHS (*Chem. Fabr.*, 1934, 7, 97—99).—Methods are described of (a) folding filter-paper for direct filtration into test tubes etc., without the use of a funnel; (b) obtaining samples of the filtrate during vac. filtration; (c) economising filter-paper; (d) effecting rapid vac. filtration with an ordinary conical funnel; (e) using the filter pump for filling pipettes; (f) erecting a simple reflux condenser (a vertical tube rests in a conical funnel placed in the neck of the distilling flask; losses are very low); (g) constructing an extremely simple self-priming glass siphon; and (h) priming siphons.

H. F. G.

Falling-sphere viscosimeter. E. SCHÖBER (*Chem. Fabr.*, 1934, 7, 113—115).—Very closely reproducible results may be obtained with a simple form of apparatus consisting of an accurately cylindrical glass tube (I) and a steel ball (II) if diameters are chosen for (I) and (II) appropriate to the material under examination. For a fall of 20 cm. the vals. may be 4.01 and 3.99 mm., respectively, for air, and 4.01 and 3.90 mm., respectively, for C₆H₆, the max. deviation (20 results) being $\pm 1.8\%$ and the mean $\pm 1.0\%$. The method may be employed at high and low pressures and for the analysis of gas mixtures.

H. F. G.

Capillary gas flow-meters. A. PINKUS (*J. Chim. phys.*, 1934, 31, 241—257).—Several instruments and auxiliary apparatus are discussed. Rates of flow between 0.2 and 10 litres per hr. are determined to within 0.2%, in general, and corrections for variations of temp. and pressure are applied by means of an empirical relation. The results generally accord with the indirect method of standardisation (cf. A., 1933, 481) but direct calibration is preferred.

J. G. A. G.

Magnetic effect on Pirani gauges using nickel wires. E. McMILLAN (*Nature*, 1934, 133, 831—832).

L. S. T.

Apparatus for determination of helium in gases. F. E. E. GERMANN, K. A. GAGOS, and C. A. NEILSON (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 215—217).—The apparatus described is a modification of that of Guye and Germann (A., 1914, ii, 740).

E. S. H.

Geochemistry.

Distribution of ozone in the atmosphere and the "Umkehrreffekt." J. GAUZIT (Compt. rend., 1934, 198, 1800—1802).—Polemical against Pekeris (Pub. Univ. Observ., Oslo, 1934, No. 9, 1). Götz' views are supported. B. W. B.

Electrical resistance of rain-water at Mulhouse. E. BANDERET and P. BOEHLER (Bull. Soc. Ind. Mulhouse, 1934, 50, 101—108).—An effort has been made to correlate the electrical resistance (E) of rain- H_2O with the time of the rainfall during the day, the intensity of the rainfall, the height of the cloud, and the season of the year, but much more numerous measurements are required to confirm the tentative conclusions. E varies widely with heat-treatments (e.g., boiling and freezing) of rain- H_2O . A. J. H.

Existence of water of abnormal density in natural conditions. G. J. VERESCHTSCHAGIN, A. I. GORBOV, and I. D. MENDELEEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 134—137).—Preliminary measurements indicate that H_2O taken from a depth of 1200 m. in Lake Baikal has d of the order of 0.00024 > that of the surface H_2O . The difference between the two diminishes on long keeping and after distillation. H. S. P.

Composition of thermal waters of Aix-les-Bains and its geological significance. A. LÉPAPE, L. MORET, and G. SCHNEIDER (Compt. rend., 1934, 198, 1706—1707).—A discussion. Data on dissolved solids and dissolved He/A ratios (I) of natural waters are quoted in support of the view that the source of Aix-les-Bains water is not Triassic. (I) is a valuable indication of the source of H_2O . B. W. B.

Nitrates in aquarium water. C. HONIG (J. Marine Biol. Assoc., 1934, [ii], 19, 723—725).—Expressed as $NaNO_3$, ≈ 1 g. per litre was found. Addition of lactate or tartrate to the H_2O stimulated denitrifying bacteria, leading to almost complete removal of NO_3' and NO_2' in the H_2O . L. D. G.

Physico-chemical characteristics of the waters of the Bay of Villefranche. P. CHAUCHARD (Compt. rend., 1934, 198, 1710—1712; cf. A., 1932, 594).—Dissolved O_2 (I) and org. matter (II) were determined in surface and deep H_2O at different points of the Bay of Villefranche. (I) showed daily evening max. due to photo-synthesis. (I) decreased and (II) increased following a storm. B. W. B.

Oxygen absorption of the lake deposit. D. MIYADI (Proc. Imp. Acad. Yokyo, 1934, 10, 236—239).— η_H falls as O_2 content falls, and is a min. when $[O_2]=0$ if the rate of absorption by mud is very great. C. W. G.

Viscosity of molten rocks. M. P. VOLAROVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1933, 1, 561—564).—By the concentric cylinder method the viscosities of Trans-Caucasian basalt (I), techenite (II) from Coursebi, andesite (III) from Casbec, diabase (IV) from Olonetz, and a mixture of (III) with 16% $Ca(OH)_2$ have been measured over the temp. range 1100—1400°. They follow the order (III) > (II) > (IV) > (I). The viscosities of (IV) and (I) become

identical above 1200°, where they both show an inflexion point, associated with crystallisation. Addition of 16% $Ca(OH)_2$ decreases the viscosity of (III) 15—20 times. J. W. S.

Composition of palygorskites. (MLLE.) S. CAILLÈRE (Compt. rend., 1934, 198, 1795—1798).—Chemical and thermal analyses, d , and n are given of specimens from a group of reputed palygorskites (I) (cf. Fersmann, A., 1913, ii, 784) which comprised: (i) serpentines from St. Gothard and Johangeorgentadt (Saxony); (ii) sepiolites from Mont Bidy (Madagascar), Portsoy, Vallecas and Dehiro (Chili); (iii) clays from Rochette près Allevard (Isère); (iv) true (I) from Kadinsk (Siberia), Nijni Novgorod, Vigan (Gord), Mevatanana (Madagascar), M'Fouati (Middle Congo), Odivellas (Portugal), and Gorbator. B. W. B.

Sodalite from Bolivia. W. BRENDLER (Amer. Min., 1934, 19, 28—31).—The dark ultramarine-blue mineral has $d^{14.5}$ 2.295, n 1.4837. Weathered sodalite is low in alkalis and Cl and high in H_2O .

CH. ABS.

Geomorphology and petrology of the Isle of Capraja. G. ROVERTO and M. AIROLDI (Mem. R. Accad. Lincei, 1934, 5, 319—410).—A very detailed account is given of a geological survey of the island, and of the results of examination of specimens of the rocks from ten different points. The rocks are notably uniform both chemically and mineralogically. The Loewinson-Lessing coeff. of acidity, α , is high, frequently 2.4—2.8. The $M_2O_3:MO$ ratio varies between 1:1.85 and 1:5.27, and the $K_2O:Na_2O$ ratio between 1:1.3 and 1:4.67. H. F. G.

Radium content of some South African granites. M. N. S. IMMELMAN (Phil. Mag., 1934, [vii], 17, 1038—1047).—An improved form of electric furnace is described, and results are tabulated for 18 specimens of granite. N. M. B.

Alteration forms of detrital staurolite etc. C. H. EDELMAN and D. J. DOUGLAS (Tsch. Min. Petr. Mitt., 1934, 45, 225—234).—The forms resulting from the corrosion of staurolite, kyanite, garnet, epidote, and sphene in detrital deposits are described. L. J. S.

Pyroxenites from the Bohemian Midland Mountains. E. TRÖGER (Tsch. Min. Petr. Mitt., 1934, 45, 209—224).—A gautelite dyke near Aussig contains enclosures of the deep-seated rocks felspar-yamaskite and felspar-jacupiringite. L. J. S.

Geochemical concealment ("Tarnung") in anomalous mixed crystals. H. SEIFERT (Tsch. Min. Petr. Mitt., 1934, 45, 191—208; cf. A., 1933, 369).—The states in which I and ClO_4 may be present in Chile saltpetre and SO_4 in limestone are discussed. L. J. S.

Activity of Komagataké in 1929. S. KÔZU (Tsch. Min. Petr. Mitt., 1934, 45, 133—174).—A large amount of newly formed dacite pumice fell as a "pumice-flow" on the sides of the mountain and as a "pumice-fall" of finer material over a wide area. It consists of 44.88% of a glassy base (n 1.494—1.497;

SiO₂ 74.07%) with embedded crystals of plagioclase, hypersthene, augite, and magnetite. Analyses are given of each of these. When heated at 450° the "flow" yields much more HCl than the "fall." At 850° the compact glassy rock expands explosively and is changed into pumice. The "flow" retained heat for a long period, and small fumaroles on its surface deposited NH₄Cl. The NH₃ for this was probably formed from atm. N₂ during the lightning discharges produced by the eruption. L. J. S.

Rôle of water in basaltic magma. II. T. C. PHEMISTER (Tsch. Min. Petr. Mitt., 1934, 45, 99—132).—Continuation (cf. this vol., 387). L. J. S.

Carboniferous dolomites of the north of France. A. BOREL (Chim. et Ind., 1934, 31, Spec. No., 272—276).—Analyses are given and modes of formation are discussed. C. W. G.

Chemical and micrographical study of a Devonian limestone. A. BOREL (Chim. et Ind., 1934, 31, Spec. No., 271).—Analyses are given. C. W. G.

Hydrothermal synthesis of kaolin. W. NOLL (Tsch. Min. Petr. Mitt., 1934, 45, 175—190).—Full details are now given (A., 1932, 716). L. J. S.

Adsorptive properties of clays in connexion with their structure. S. S. URAZOVSKI and M. M. SCHTSCHERBAK (Ukrain. Chem. J., 1933, 8, 155—167).—The adsorptive capacity (I) for C₆H₆ vapour of Tschasov Jar and Vladimirov kaolins increases on

preheating to a max. at 500°, and falls almost to 0 at 1000°. A quant. connexion exists between diameter of pores and (I) of a given clay. R. T.

Conclusions derived from the gravitation measurements carried out in the Emba district. V. P. SKVORTZOV (Nef. Choz., 1933, 25, No. 10, 14—17).—The relation between geological formation and oil deposits is discussed. CH. ABS.

Genesis of the Central Asiatic petroleum deposits. V. B. PORFIRIEV and V. A. VASILIEV (Nef. Choz., 1933, 25, No. 10, 18—22).—A discussion. CH. ABS.

Rare gases of the sub-soil of Lille. L. DOLLÉ (Chim. et Ind., 1934, 31, Spec. No., 277—278).—He, A, Kr, and Xe are comparatively abundant. C. W. G.

Classification of forest humus types by means of their catalytic power. W. GÜNTHER (Z. Pflanz. Düng., 1934, A, 34, 30—89).—The catalytic power (I) of soils is not necessarily shown by the total O₂ liberated during a definite period. The rate of evolution of O₂ varies considerably with time and the whole course of the reaction should be examined. Vals. obtained are influenced by the H₂O content of the sample, the ratio of soil to H₂O₂ used, and temp. (approx. const. over the range 15—20°). Appropriate technique for determining (I) is established. A system of classification of forest humus accumulations, based on the form of the catalytic curves, is described. A. G. P.

Organic Chemistry.

Controlled oxidation of methane under pressure. A. PARIS (Chim. et Ind., 1934, 31, Spec. No., 411—420).—The influence of temp., pressure, and amount of O₂ on the process has been studied. The main products of the oxidation are MeOH, CO₂, and H₂O. The isolation of MeOH in appreciable quantities is rendered possible owing to the preferential increase with pressure of the speed of the reaction CH₄+0.5O₂=MeOH, compared with other possible reactions. The best yields of MeOH are obtained when the % of O₂ in the mixture is low and the temp. > 450°. The process does not appear to be practicable industrially owing to the large quantities of gas which must be circulated relative to the yield of MeOH obtained. H. S. P.

Preparation of ethane. S. GLASSTONE and A. HICKLING (Chem. and Ind., 1934, 23, 512).—The statement that C₂H₆ can be prepared (along with 2 vols. of CO₂) by warming Ac₂O with BaO₂ seems to be misleading. The reaction is often violent whether Ac₂O or AcOH is used and little C₂H₆ is produced. C. I.

Preparation of normal heptane. C. H. KAO and W. S. CHANG (J. Chinese Chem. Soc., 1934, 11, 18—20).—Heptyl bromide with a Zn couple in boiling 85% EtOH during 18 hr. affords *n*-heptane (76%), which cannot be prepared from heptaldehyde. Zn-Hg, and HCl (cf. A., 1913, i, 733). J. L. D.

Hexamethylethane. D. T. FLOOD and G. CALINGAERT (J. Amer. Chem. Soc., 1934, 56, 1211—1212).—CMe₃·CMe₃, m.p. 100.7—101.4°, is obtained in 10% yield when Mg is added to Bu^γCl in boiling Et₂O containing a little I. The main products of the reaction are *isobutene* and *isobutane*; a little *βββ*-trimethylpentane is also formed. H. B.

Preparation of ethylene and its homologues by cracking heptane in presence of water vapour. C. MATIGNON and M. SÉON (Compt. rend., 1934, 198, 1649—1652).—C₇H₁₆ (I) at 700° in a quartz tube affords very little C₂H₄ (II), but mainly its homologues (III) (39%). At 900°, when H₂O:(I) is 2.7:1 about 42% of (II) is formed, and at 935°, when H₂O:(I) is 5.2:1, 62% of (II) results. (III) is much reduced in presence of H₂O vapour. J. L. D.

Peroxide effect in addition of reagents to unsaturated compounds. V. Addition of hydrogen bromide to Δ^α-butene. VI. Addition of hydrogen bromide to *isobutene*. M. S. KHARASCH and J. A. HINCKLEY, jun. (J. Amer. Chem. Soc., 1934, 56, 1212—1214, 1243—1245).—V. Addition of HBr to Δ^α-butene (I) in presence or absence of air, in AcOH, or in presence of anti-oxidants gives 70—90% yields of *sec*-BuBr, which is considered to be the normal product. In presence of 0.06—0.1 mol. of ascaridole, a 76—95% yield of Bu^αBr (the abnormal product) is obtained. If air or O₂ is passed through

(I) at -80° for 2 hr. no peroxide is formed. External effects (solvent, temp., light) affect the peroxide-catalysed reaction only.

VI. Addition of HBr to *isobutene* in absence or presence of air, in AcOH or xylene, or in presence of anti-oxidants gives 85—95% yields of Bu^vBr (the normal product). In presence of ascaridole (0.03—0.04 mol.) a mixture of Bu^βBr (80—90%) and Bu^vBr (10—20%) results. Temp. and light have no effect on the normal reaction. H. B.

Reaction of bromine with ethylene derivatives in methyl alcohol. I. K. MENDEL (Annalen, 1934, 510, 129—155).—The ratio Br : OMe in the products formed from the following compounds and a 5% solution of Br in MeOH containing 5% of CaBr₂ is: *cyclohexene* (I), 3.48 : 1 (2.66 : 1 in absence of CaBr₂); *allylbenzene*, 4.62 : 1; *anethole* (II) 1.1 : 1 (the *p*-OMe group being disregarded); *isosafole*, 1.16 : 1; CH₂:CPh₂, 1.34 : 1. More OMe is added when the C:C linking is conjugated with the C₆H₆ ring. (I) affords a mixture of 1 : 2-dibromo- (III) and 1-bromo-2-methoxy- (IV) *-cyclohexane*; subsequent reduction (H₂, Pd-BaSO₄, MeOH-NaOH) removes (III). The resultant (IV), b.p. 76°/10 mm., and AgOAc-AcOH give [after hydrolysis (MeOH-conc. HCl)] 2-methoxy-*cyclohexanol*, b.p. 49°/0.3 mm. (II) does not yield any dibromide but gives a mixture (A) of about 95% of *p*-OMe-C₆H₄·CH(OMe)·CHMeBr and 5% of *p*-OMe-C₆H₄·CH(OMe)·CHMe·OMe. Treatment of (A) with NaOEt and subsequent hydrolysis (HCl) gives *p*-OMe-C₆H₄·COEt (*oxime*, m.p. 72—73°), whilst reduction (Zn dust, MeOH) affords impure (II) [Br-derivative dibromide, m.p. 111° (lit. 108°)]. β-*Hydroxy-α-methoxy-α-anisylpropane*, b.p. 112°/0.35 mm., is obtained from (A) and KOAc-AcOH followed by hydrolysis (MeOH-conc. HCl); a small amount of a ketone (semicarbazone, m.p. 188°) is also formed.

The "Br-binding nos." (A., 1932, 717) of 28 unsaturated substances are determined using 5% MeOH-Br containing 5% CaBr₂; with the exception of safole, C₂H₄ has the highest val. Compounds containing C:C conjugated with the C₆H₆ ring give vals. < 67, whilst the non-conjugated substances show vals. > 67. The val. for (I) decreases if a more dil. solution of Br is used (concn. of MeOBr being thereby increased) or if the CaBr₂ is omitted (decrease in the concn. of Br'). H. B.

Acetylene polymerides and their derivatives.

XIX. Structure of divinylacetylene polymerides. M. E. CUPERY and W. H. CAROTHERS (J. Amer. Chem. Soc., 1934, 56, 1167—1169).—Divinylacetylene (I) (A., 1932, 40) heated at 80° in N₂ gives an oily polymeride (II) (*M* about 230), separable from unchanged (I) by evaporation of (I) in a vac. (II) and Br in cold CCl₄ afford a compound, C₁₂H₁₂Br₆, and (II) [from (I) in presence of a little pyrogallol at 81—82°] carefully distilled at 0.1 mm. in N₂ gives a compound (III), C₁₂H₁₂, b.p. 53—55°/about 1 mm. (*octa-*, m.p. 137°, and *deca-*, m.p. 211°, *-bromides*), which is oxidised by alkaline KMnO₄ at 50—60° to *trans-cyclobutane-1:2-dicarboxylic acid* (IV), H₂C₂O₄, succinic acid, and an oily acid; oxidation in the cold affords (IV) and (probably) a hydroxycyclobutane-carboxylic acid (*p*-*bromophenacyl ester*, m.p. 145°).

(II) is a mixture of EtOH-sol. and -insol. products; reduction (H₂, PtO₂, EtOH) of the former gives products, b.p. 36—38°/about 0.1 mm., and 38—40°/about 0.1 mm., with the composition C₁₂H₂₄, and a fraction, b.p. 111—113°/1—1.5 mm., composition C₁₈H₂₄. (III) is represented as 1 : 2-*di(vinylacetylenyl) cyclobutane*. H. B.

Preparation of alkyl bromides. I. C. L. TSENG and C. S. HOU (J. Chinese Chem. Soc., 1934, 11, 57—72).—Interaction of alcohols with PBr₃ affords a better yield of Br-compound than when a mixture of P and Br is used, although yields are best when HBr is used. J. L. D.

Addition of hydrogen bromide to Δ^β-pentene. W. M. LAUER and F. H. STODOLA (J. Amer. Chem. Soc., 1934, 56, 1215—1218).—Δ^β-Pentene (I) [prepared by the method of Sherrill *et al.* (A., 1929, 1419) or from CHBrMe·CHEt·CO₂H (synthesis described) and aq. Na₂CO₃ (cf. Fittig and Howe, A., 1880, 375)] and HBr in absence or presence of AcOH give a mixture of approx. equal amounts of β- and γ-bromopentanes. Analysis is effected by converting the mixtures into Grignard reagents, treatment with PhNCO, and subsequent thermal analysis of the mixture of anilides so produced. The results do not conform with the rule of Wagner and Saytzeff (A., 1876, i, 547). It is considered that current views regarding electromeric displacements in (I) must be modified. H. B.

Preparation of octyl alcohol and methyl hexyl ketone from Chinese castor oil. C. H. KAO and J. Y. YEN (J. Chinese Chem. Soc., 1934, 11, 21—31).—When castor oil soap (prep. described) is heated a mixture of octyl alcohol (I) and Me hexyl ketone (II) is obtained, separated by interaction with *o*-C₆H₄(CO)₂O at 110° into a *sec.*-octyl phthalate [decomposed by NaOH into pure (I)] and pure (II) (also obtained from (I) with boiling Na₂Cr₂O₇-H₂SO₄ during 4 hr.) which when reduced with Na in H₂O affords (I) admixed with traces of neutral hydrocarbons. Sebacic acid is always formed in this reaction. J. L. D.

Preparation of methylethylamylcarbinol, methylethylamylcarbonyl iodide, δ-methyloctan-γ-ol, and γ-bromo-δ-methyloctane. J. H. GREEN (J. Amer. Chem. Soc., 1934, 56, 1167).—Me *n*-amyl ketone and MgEtBr give *methylethyl-n-amylcarbinol*, b.p. 36—37°/3 mm. (*iodide*, b.p. 58°/5 mm.). β-Bromo-hexane, b.p. 142—144° (from CHMeBu^α-OH), Mg, and EtCHO in cold Et₂O afford δ-*methyloctan-γ-ol*, b.p. 132—133°/20 mm. (*bromide*, b.p. 180°). H. B.

Abnormal reaction of hypochlorous acid with dimethylpentenol. (MLLE.) M. VEILER (Compt. rend., 1934, 198, 1704—1705).—Interaction of βδ-dimethyl-Δ^γ-penten-β-ol with HOCl affords the chlorohydrin and γ-chloro-βδ-dimethylpentane-αβδε-tetraol (?), m.p. 132° (hydrolysed by K₂CO₃ to a Cl-free substance), together with γ-chloro-βδ-dimethyl-Δ^β-penten-β-ol, b.p. 47°/10 mm. J. L. D.

Dehydration of tert-butyl-tert-heptylcarbinols. I. N. NAZAROV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 85—88).—Ditert-butylcarbinol undergoes dehydration and fission in presence of anhyd. H₂C₂O₄ (I) at 120—130° (cf. A., 1933, 1271).

Pinacolin, NH_2Na , and EtI give readily di- and, with difficulty in boiling C_6H_6 , tri-ethylpinacolin (40—50% yield), reduced by Na-EtOH to $\beta\beta$ -dimethyl- $\delta\delta$ -diethyl-hexan- γ -ol, b.p. 225—228°, dehydrated by (I) at 140—160° to a little CMe_2CHMe , more $\text{CHMe}\cdot\text{CEt}_2$, and much of a mixture (II) of dodecenes. $\text{OH}\cdot\text{CHBu}^\gamma\cdot\text{CMe}_2\text{Bu}^\gamma$ gives, however, only (II).

R. S. C.

Complexes of mannitol and sorbitol with sodium arsenite and borax.—See this vol., 741.

Ethoxy-derivatives of α -glycols of high mol. wt. D. BARDAN (Bull. Soc. chim., 1934, [v], 1, 141—146).—Hexoyl chloride with excess of Br affords α -bromohexoyl chloride, b.p. 110—112°/33 mm., converted by EtOH and NaOEt into *Et* α -ethoxyhexoate (I), b.p. 98—101°/22 mm. Similarly prepared, α -bromo-octoyl chloride has b.p. 129—133°/25—26 mm. and *Et* α -ethoxyoctoate (II), b.p. 134—137°/31 mm. Interaction of (I) and (II) with excess of the necessary Mg alkyl compound (cf. A., 1932, 41) affords γ -ethoxy- β -methylheptan- β -ol, b.p. 100—102°/28 mm.; γ -hydroxy- δ -ethoxy- γ -ethyl-octane, b.p. 128—129°/45 mm., and -decane, b.p. 143—148°/33—34 mm.; δ -hydroxy- ϵ -ethoxy- δ -n-propyl-nonane, b.p. 141—145°/27—28 mm., and -undecane, b.p. 171—175°/35—37 mm.; ϵ -hydroxy- ζ -ethoxy- ϵ -n-butyl-decane, b.p. 164—167°/27 mm., and -dodecane, b.p. 189—193°/34 mm.; α -hydroxy- β -ethoxy- α -diphenyl-hexane, m.p. 57.5°, and -octane, m.p. 38.5—39°, respectively. J. L. D.

Alcoholysis of glyceryl triacetate in feebly alkaline media.—See this vol., 737.

Unexpected formation of glycerol- β -phosphoric acid. O. BAILLY and J. GAUMÉ (Compt. rend., 1934, 198, 1932—1934).— Na_2MePO_4 and epichlorohydrin give the mixed Na ester, which with hot aq. KOH yields glycerol- β -phosphoric acid.

R. S. C.

Synthesis of dihydroxyacetonephosphoric acid. W. KIESSLING (Ber., 1934, 67, [B], 868—874).—Treatment of $\text{CO}(\text{CH}_2\cdot\text{OH})_2$ in quinoline with POCl_3 leads mainly to dihydroxyacetonediphosphoric acid (I) at 0—10°, whereas at -15° to -20° the monophosphoric acid (II) is almost exclusively formed. (I) is unstable in acid and, probably, in alkaline solution, and does not yield PO_4''' under the influence of N-NaOH . (II) is isolated as the *Ca* salt (III) $\text{C}_5\text{H}_5\text{O}_6\text{PCa}_2\cdot 0.5\text{H}_2\text{O}$ (also compound $\text{C}_3\text{H}_5\text{O}_6\text{PCa}_2\cdot\text{HSO}_3\text{Ca}_{0.5}$) and *Ba* salt (IV). (III) and (IV) decompose slowly when preserved or in neutral solution into PO_4''' and polymerisation and condensation products. Like other triosephosphoric acids (V), (II) is converted by N-HCl at 100° into AcCHO and PO_4''' , and by N-NaOH at 15—20° into PO_4''' and $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$. The acid hydrolysis curve of (II) is closely similar to that of glyceraldehydephosphoric acid (VI). Unlike (VI), but similarly to (V), (II) is unchanged by I, and only slightly changed by Br . With dinitrophenylhydrazine (II) gives products containing P and consisting mainly of methylglyoxal-oxazone. (II) is largely fermented and exhibits the enzymic equilibrium (II) \rightleftharpoons hexosediphosphoric acid. It is considered that (VI) consists mainly, (V) entirely, of (II). H. W.

Partly acylated sugar alcohols. IV. Structure of the *p*-toluenesulphonyl derivatives of mannitol $\alpha\zeta$ -dibenzoate. A. MÜLLER (Ber., 1934, 67, [B], 830—835; cf. A., 1933, 931).—Anhydromannitol $\alpha\zeta$ -dibenzoate di-*p*-toluenesulphonate in CHCl_3 is hydrolysed by NaOMe-MeOH to anhydromannitol di-*p*-toluenesulphonate, m.p. 129—130°, $[\alpha]_D^{20} +38.2^\circ$ in CHCl_3 , which, with NaOAc and Ac_2O , gives the corresponding $\alpha\zeta$ -diacetate, m.p. 86°, $[\alpha]_D^{20} +52.9^\circ$ in CHCl_3 , and, with *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ and $\text{C}_5\text{H}_5\text{N}$ at 15—20°, gives the $\alpha\zeta\text{xx}$ -tetra-*p*-toluenesulphonate, m.p. 170° after softening at 168°, $[\alpha]_D^{20} +48.0^\circ$ in CHCl_3 , which rapidly yields $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Na}$ with anhyd. NaI in COMe_2 at 130°. Dianhydromannitol *p*-toluenesulphonate, *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$, and $\text{C}_5\text{H}_5\text{N}$ at 15—20° afford dianhydromannitol ζx -di-*p*-toluenesulphonate, m.p. 100°, $[\alpha]_D^{20} -28.6^\circ$ in CHCl_3 , transformed by anhyd. NaI in COMe_2 at 130° into dianhydromannitol *p*-toluenesulphonate ζ -iodohydrin, m.p. 121—122°, $[\alpha]_D^{20} -68.3^\circ$ in CHCl_3 , which, with AgF in $\text{C}_6\text{H}_6\text{N}$, gives dianhydro- Δ^4 -mannitene *p*-toluenesulphonate, m.p. 80° after softening at 65°, $[\alpha]_D^{20} -66.5^\circ$ in CHCl_3 . Mannitol $\gamma\epsilon$ -diacetate $\alpha\zeta$ -dibenzoate $\beta\delta$ -di-*p*-toluenesulphonate is hydrolysed by NaOMe-MeOH to mannitol $\beta\delta$ -di-*p*-toluenesulphonate, m.p. 157° (decomp.), $[\alpha]_D^{20} +20.0^\circ$ in $\text{C}_5\text{H}_5\text{N}$ (whence mannitol tetra-benzoate $\beta\delta$ -di-*p*-toluenesulphonate, m.p. 153° after softening at 150°, $[\alpha]_D^{20} +41.6^\circ$ in CHCl_3), oxidised by $\text{Pb}(\text{OAc})_4$ to CH_2O and *d*-arabinose $\beta\delta$ -di-*p*-toluenesulphonate, m.p. 168°, $[\alpha]_D^{20} -14.7^\circ$ in $\text{C}_5\text{H}_5\text{N}$. *d*-Sorbitol $\alpha\zeta$ -dibenzoate, *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$, and $\text{C}_5\text{H}_5\text{N}$ at 40° give anhydro-*d*-sorbitol $\alpha\zeta$ -dibenzoate di-*p*-toluenesulphonate, m.p. 123.5°, $[\alpha]_D^{20} +66.35^\circ$ in CHCl_3 .

H. W.

Meltzer's reaction and detection of ether peroxide. A. CASTIGLIONI (Annali Chim. Appl., 1934, 24, 209—212).—With the Et_2O extract of a soap, Meltzer's reaction (A., 1898, ii, 650) as modified by Kreis (A., 1899, ii, 827) gave an eosin-red colour, traceable to the presence of "peroxide" in the Et_2O used. To detect the "peroxide," 1—2 c.c. of the Et_2O is evaporated in a porcelain dish and to the residue are added a drop each of 95% EtOH , PhCHO , and conc. H_2SO_4 ; an eosin-red colour shows "peroxide" with certainty. T. H. P.

Acetylene polymerides and their derivatives. XX. Addition of alcohols to vinylacetylene. R. A. JACOBSON, H. B. DYKSTRA, and W. H. CAROTHERS (J. Amer. Chem. Soc., 1934, 56, 1169—1170).— $\text{CH}_2\text{:CH}\cdot\text{C}\equiv\text{CH}$ and ROH in presence of NaOR at about 100° give $\text{CMe}\text{:C}\cdot\text{CH}_2\cdot\text{OR}$ (I); $\text{CH}_2\text{:C}\equiv\text{C}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OR}$ is probably an intermediate and is converted by NaOR into (I). The following are described: *Me* (II), b.p. 99.5—100°, *Et* (III), b.p. 119—120°, *Pr* ^{β} , b.p. 132—134°, *Bu* ^{α} , b.p. 161—162°, *Bu* ^{γ} , b.p. 125—135°, cyclohexyl, b.p. 64°/2 mm., benzyl, b.p. 94—96°/3 mm., β -hydroxyethyl, b.p. 71—73°/4 mm., and β -methoxyethyl, b.p. 84—87°/30 mm., Δ^{β} -butinenyl ethers. (II) and (III) are reduced (H_2 , PtO_2 , AcOH) to MeOBu^α and EtOBu^α , respectively; (II) is oxidised (alkaline KMnO_4 at 35—40°) to AcOH and $\text{OMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

H. B.

Preparation of primary *n*-alkyl sulphates. C. BARKENBUS and J. J. OWEN (J. Amer. Chem. Soc.,

1934, 56, 1204—1206).— $\text{ClSO}_2\cdot\text{OR}$ (from SO_2Cl_2 and ROH) and $\text{SO}(\text{OR})_2$ (from SOCl_2 and ROH) at $115\text{--}140^\circ$ in absence or presence of ZnCl_2 give R_2SO_4 (cf. Levailant, A., 1933, 1274). The following are described: *Bu*^a, b.p. $97.4^\circ/3$ mm., *n*-amyl, b.p. $117^\circ/2.5$ mm., *n*-hexyl, b.p. $125.3^\circ/2$ mm., *n*-heptyl, b.p. $146.6^\circ/1.5$ mm., m.p. 11.4° , *n*-octyl, b.p. $166.1^\circ/2$ mm., m.p. 20.3° , *n*-nonyl, m.p. $41.9\text{--}42.1^\circ$, *n*-decyl, m.p. $37.6\text{--}37.8^\circ$, *n*-dodecyl, m.p. $48.4\text{--}48.5^\circ$, *n*-tetradecyl, m.p. $57.8\text{--}58^\circ$, *n*-hexadecyl, m.p. $66.2\text{--}66.3^\circ$, and *n*-octadecyl, m.p. $70.2\text{--}70.7^\circ$, sulphates. All b.p. and m.p. are corr. The method does not appear to be applicable to branched-chain primary, *sec.*-, or *tert.*-alcohols.

H. B.

Enzymic equilibrium between hexosediphosphoric acid and dihydroxyacetonephosphoric acid. See this vol., 807.

Synthetic glycerides. V. Mixed triglycerides of the dilaurin series. O. E. McELROY and C. G. KING (J. Amer. Chem. Soc., 1934, 56, 1191—1192).—The following *sym.*-glycerides (I) are prepared from α -dilaurin and the requisite acyl chloride in quinoline, whilst the *as.*-isomerides (II) are obtained similarly from glyceryl α -acylate and lauryl chloride: α -, m.p. 44.8° , and β -, m.p. 47.8° , -palmityl-; α -, m.p. 42.8° , and β -, m.p. 50.2° , -myristyl-; α -, m.p. 32.6° , and β -, m.p. 38.8° , -deco-; α -, m.p. 28.4° , and β -, m.p. 30.2° , -octo-dilaurins. α -, m.p. 55.2° , and β -, m.p. 62° , -Acetyldistearins and β -butyryldistearin, m.p. 51° , are described. (I) generally have higher m.p., higher *n*, and lower solubilities than (II) (cf. A., 1932, 364).

H. B.

Relation of m.p. to the number of carbon atoms in normal mercaptans. D. E. TEETS (J. Amer. Chem. Soc., 1934, 56, 1143—1144).—The m.p. of the following RSH are determined essentially by the method of Andrews *et al.* (A., 1925, ii, 852): R=Me, -123.1° (lit. -121°); Et, -147.3° ; Pr, -113.3° (lit. -115.5°); Bu, -115.9° ; amyl, -75.7° ; hexyl, -81.03° ; heptyl, -43.4° ; octyl, -49.2° ; nonyl, -20.1° ; alternation is exhibited. When the log. of the mol. wt. is ≤ 2 , the m.p. lie on a straight line (cf. Austin, A., 1930, 675). Austin's relationship (*loc. cit.*) between *m.p.* and mol. wt. does not hold if the mol. wt. is < 100 .

H. B.

Influence of dipole moment on the number of molecules of a base fixed by a salt. A. ABLOV (Compt. rend., 1934, 198, 1789—1791).—By evaporation of EtOH solutions of the components at room temp. $(\text{CCl}_3\text{CO}_2)_2\text{Ni}$ forms additive compounds of the type $+4\text{NH}_2\text{Ar}$ with NH_2Ph (I), *o*- (II) $+ \text{H}_2\text{O}$, *m*- (III), and *p*- (IV) $-\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, *o*- (V) and *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, *o*- $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ (VI), and *m*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$; of the type $+3\text{NH}_2\text{Ar}$ with *o*- and *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$; of type $+5\text{NH}_2\text{Ar}$ with *p*- $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$; and of type $+6\text{NH}_2\text{Ar}$ with *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ (VII) and *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$ (VIII). $(\text{CHCl}_2\text{CO}_2)_2\text{Ni}$ gives additive compounds of type $+4\text{NH}_2\text{Ar}$ with (I), (III), (IV), [no compound with (II) and (VI)]; of type $+2\text{NH}_2\text{Ar}$ with (V) $+0.5\text{H}_2\text{O}$; of type $+5\text{NH}_2\text{Ar}$ with (VII); and of type $+6\text{NH}_2\text{Ar}$ with (VIII).

J. W. B.

Effect of the α -nitro-group in three-carbon tautomerism.—See this vol., 772.

Structure of acids obtained by oxidation of triisobutene. I. β -Acid of Conant and Wheland. F. C. WHITMORE and K. C. LAUGHLIN (J. Amer. Chem. Soc., 1934, 56, 1128—1130).—The acid $\text{C}_{12}\text{H}_{24}\text{O}_2$, m.p. 129° (prep. described), of Conant and Wheland (A., 1933, 804) is methyltert-butylneopentylacetic (α -*xy*-trimethyl- α -tert-butylvaleric) acid (I), and is probably formed from $\beta\beta\delta\zeta\zeta$ -pentamethyl- Δ^7 -heptene (cf. McCubbin, A., 1931, 333) by addition of neutral O (electron sextet) to the pair of electrons in the activated double linking. The acid chloride [hydrolysed to (I) with m.p. $130\text{--}130.5^\circ$] and NaN_3 in PhMe give [after hydrolysis (HCl)] an amine (hydrochloride, m.p. $215\text{--}217^\circ$), which with HNO_2 affords methyltert-butylneopentylcarbinol, b.p. $61^\circ/6$ mm., m.p. $10\text{--}11^\circ$ (chloride, b.p. $72.5\text{--}74^\circ/8$ mm.), also prepared from Bu^v neopentyl ketone and MgMeI . The α -acid of Conant and Wheland does not possess either of the structures suggested (*loc. cit.*).

H. B.

p-Phenylphenacyl esters of the hexoic acids. F. WREDE and A. ROTHHAAS (Ber., 1934, 67, [B], 739—740).—The acid is neutralised with 1% NaOH and the solution rendered just acid, mixed with a suspension of *p*- $\text{C}_6\text{H}_4\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\text{Br}$ in EtOH, and boiled for 1 hr. The esters, which separate from the cooled solution, are well adapted for the identification of the acids. *p*-Phenylphenacyl *n*-hexoate (I), m.p. $69\text{--}70^\circ$, γ -methylvalerate (II), m.p. $69\text{--}70^\circ$, *r*- β -methylvalerate, m.p. 47° , *r*- α -methylvalerate, m.p. 46° , *r*- α - β -dimethylbutyrate, m.p. 73.5° , α -dimethylbutyrate, m.p. 86.5° , $\beta\beta$ -dimethylbutyrate, m.p. 92° , and α -ethylbutyrate, m.p. 77.5° , are described. *n*-Hexoic and γ -methylvaleric acid are best distinguished as their amides, m.p. 100° and 119° , respectively, obtained by heating the NH_4 salts in sealed tubes at 250° for 5 hr. (I) and (II) do not give a depression of m.p. when mixed. $\text{CH}_2\text{Bu}^v\cdot\text{CO}_2\text{H}$ is obtained by allowing Bu^vI to react with $\text{CHNa}(\text{CO}_2\text{Et})_2$ during several days at room temp., then heating to boiling, and proceeding as usual.

H. W.

p-Substituted phenacyl esters of *trans*-olefinic acids. W. KIMURA (J. Soc. Chem. Ind. Japan, 1934, 37, 154—156B; cf. A., 1932, 946).—Interaction of the *trans*-olefinic acid with *p*-substituted phenacyl bromides affords the following *trans*-compounds: *p*-chloro-, m.p. 56° , *p*-bromo-, m.p. 65° , *p*-iodo-, m.p. 74° , and *p*-phenyl-phenacyl elaidate, m.p. 73.5° ; *p*-chloro-, m.p. 69.5° , *p*-bromo-, m.p. 74.2° , *p*-iodo-, m.p. 84° , and *p*-phenyl-phenacyl brassidate, m.p. 85.6° ; *p*-chloro-, m.p. 69.5° , *p*-bromo-, m.p. 74° , *p*-iodo-, m.p. 82° , and *p*-phenyl-phenacyl cetelaidate, m.p. 84.5° . J. L. D.

Olefinic acids. XII. β -Phenylhexenoic and β -methylpentenoic acids.—See this vol., 770.

Polymerisation of methyl esters of higher unsaturated fatty acids. XIII. Action of halogens on the polymerised ester. K. KINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 25—32).—The I vals. of polymerides (I) prepared from linoleic acid (II) and higher unsaturated fatty acids in H_2 during several hr. at $280\text{--}290^\circ$ increase with the time of contact with the halogen. (I) absorb Br, which is easily removed with $\text{Zn}\text{--}\text{HCl}\text{--}\text{MeOH}$, but very little depolymerisation occurs with (I) from (II);

the (I) of clupanodonic acid is depolymerised about 40%. The four-membered rings formed in (I) are unattacked by Br; besides substitution, addition occurs at the double linkings which results in high I and Br vals. in protracted reactions. J. L. D.

Hofmann degradation of α -methoxy-acids. F. MICHEEL and K. KRAFT (Ber., 1934, 67, [B], 841—844).—The degradation of lact-, α -methoxypropion-, (I), mandel-, α -methoxyphenylacet-, glucon-, and the corresponding $\alpha\beta\delta$ -Me₄-amide by NaOCl under Weerman's conditions occurs with formation of aldehyde and CNO'. Detection of CNO' is not a certain criterion of the presence of α -OH. The more rapid reaction of the OH-amide and the greater quantity of CNO' produced permits discrimination between α -OH- and α -OMe-acids. Degradation of (I) in presence of much MeOH gives a compound (?) OMe·CHPh·NH·CO₂Me, m.p. 67°, immediately decomposed by acid with production of PhCHO. H. W.

Electrolytic oxidation of β -hydroxypropionic acid.—See this vol., 739.

Acetoacetic ester condensation. VI. Mechanism of the reaction. R. F. B. COX, E. H. KROEKER, and S. M. McELVAIN (J. Amer. Chem. Soc., 1934, 56, 1173—1178).—Et α -isobutyryl- β -phenylpropane- $\alpha\gamma\gamma$ -tricarboxylate does not lose EtOH when heated to 250° (much decomp. occurs); in presence of NaOEt (1 mol.) at 120°, Et 5-phenyl-2 : 2-dimethylcyclohexane-1 : 3-dione-4 : 6-dicarboxylate, m.p. 144—145°, is obtained in 42% yield, as the result of an internal acetoacetic ester condensation (cf. Dieckmann and Kron, A., 1908, i, 388). Et α -methylglutarate (I) (1 mol.), Et₂C₂O₄ (2 mols.), and NaOEt (1 mol.) at 125—130° give 37% of Et butane- $\alpha\alpha\gamma$ -tricarboxylate [formed by loss of CO from the intermediate CO₂Et·CO·CH(CO₂Et)·CH₂·CHMe·CO₂Et]; Et 3-methylcyclopentane-1 : 2-dione-3 : 5-dicarboxylate is not produced [in agreement with Dieckmann (A., 1899, i, 676)]. Et α -methylacrylate and Et isobutyrylacetate (II) in EtOH-NaOEt give Et α -isobutyryl- α' -methylglutarate, b.p. 144—147°/10 mm., which with NaOEt (1 mol.) at 115—125° affords EtOH (0.85 mol.), (II) (0.63 mol.), and a little (I); a cyclic condensation product is not formed. A mechanism for the acetoacetic ester condensation must explain (i) condensation between the CO₂Et of a simple ester and a C atom attached to 2H and a negative group (CO₂Et, CN, acyl), (ii) condensation between CO₂Et which is part of a C(CO₂Et)₂ group and a C atom to which is attached a negative group and only 1 H. An extension of Michael's mechanism (A., 1888, 1054) is favoured: 2EtOAc → OEt·CMe(OH)·CH₂·CO₂Et ⇌ OH·CMe·CH·CO₂Et + EtOH. H. B.

Compounds of uranyl oxalate with alkaline-earth oxalates. A. COLANI (Compt. rend., 1934, 198, 1510—1512; cf. A., 1917, i, 513, 535).—UO₂C₂O₄ (I) and CaC₂O₄ do not react in H₂O at 15° or 50°. (I) with SrC₂O₄ at 15° and 50° affords UO₂Sr(C₂O₄)₂·4H₂O, and with BaC₂O₄ it affords UO₂Ba(C₂O₄)₂·5H₂O and UO₂Ba₂(C₂O₄)₃·7H₂O. J. L. D.

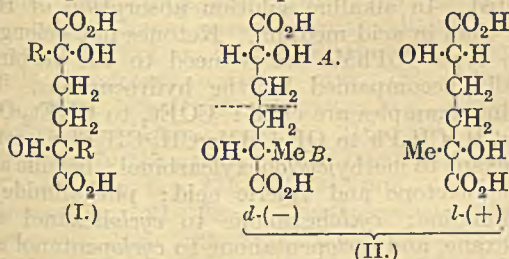
Ethyl Δ^1 -cyclopentenylmalonate. G. A. R. KON and Z. T. LING (J.C.S., 1934, 596—599).—Work previously described (A., 1930, 773) is repeated and amplified. cyclopentenylidenemalonic acid (A., 1926, 1246) [Et ester (I), b.p. 138—141°/10 mm., prepared by the Ag salt method (A., 1932, 252)] with (i) 2N- and (ii) 0.7N-EtOH-HCl at room temp. for 1 week gives (mainly) Et Δ^1 -cyclopentenylmalonate (II), with (i) b.p. 150°/17 mm., I addition (method; A., 1931, 608) 41.5%, and (ii) b.p. 136°/10 mm., I addition 44.9%. Decomp. of the solid K derivative obtained from (II) and dry KOEt in light petroleum with Et₂O-BzOH gives the ester (A) with b.p. 140°/15 mm., I addition 57.3% [indicating that the min. $\beta\gamma$ -content of (A) is 57.3%; the actual val. is undoubtedly much higher, since esters of this type react slowly and incompletely with ICl]. (I) has no measurable I addition. Attempted reduction (Al-Hg, moist Et₂O) of (A), in the hope of converting the $\alpha\beta$ -ester present into a bimol. product, results in an increase in the amount of $\alpha\beta$ -form present. Refractometric data for (I), (A), and Et α -methyl- Δ^1 -cyclopentenylmalonate, b.p. 146°/11 mm., I addition 43.3%, indicate that the max. amount of $\alpha\beta$ -ester in (A) is 18%. Similar data also indicate that the Et Δ^1 -cyclohexenylmalonate, b.p. 150°/14 mm., I addition 23.5%, prepared by the Ag salt method, is not a pure $\beta\gamma$ -ester; the $\beta\gamma$ -content of the ester, b.p. 154°/16 mm., I addition 32%, obtained by esterification with cold 2.2N-EtOH-HCl, is of the same order as that of (A) and is not increased by regenerating the ester from its K derivative. Et α -methyl- Δ^1 -cyclohexenylmalonate has b.p. 155.5°/16 mm., I addition 42.7%. All attempts to convert Et α -cyanocyclohexylideneacetate into the $\beta\gamma$ -form have been unsuccessful. K derivatives (as above) have the anionic charge localised on O. Treatment with a non-ionised polar mol. (e.g., alkyl iodide) causes redistribution of the charge to C α and an α -alkyl derivative is formed. Acidification with aq. acid causes redistribution of the charge within the anion and both $\alpha\beta$ - and $\beta\gamma$ -forms are produced (according to their respective stabilities). Acidification with a weak org. acid in a neutral solvent may not bring about redistribution of the charge beyond C α . Tautomerism in compounds such as the above is best considered as three-carbon and not pentad keto-enol (Shoppee, A., 1928, 1240). Enolisation frequently facilitates, but is not essential to, tautomerism. H. B.

Walden inversion. II. Mutual transformation of the tartaric acids by means of Walden's inversion; attempt to transform mesotartaric acid into active tartaric acids. V. A. RAO and P. C. GUHA (Ber., 1934, 67, [B], 741—749).—Et mesotartaric acid (I) is converted by PCl₅ in CHCl₃ at 65—70° into Et chlorohydroxysuccinate, b.p. 147—150°/13 mm., transformed by Ag₂O-H₂O into mesotartaric acid (II), but not affected by Pb(OH)₂. For the determination of (II) in presence of *r*- (III) or *d*- (IV) -tartaric acid, the suitably conc. solution is divided into two equal portions, one of which is exactly neutralised with KOH, mixed with EtOH-AcOH (3 : 1 vol.), and added to the other portion. After 1 day the pptd. *r*- or *d*-C₄H₅O₆K is collected, dried,

and weighed, and (II) is determined in the filtrate as the Ba or Pb salt. Treatment of *l*-chlorohydroxy-succinic acid with Pb(OH)₂ yields exclusively (II), whereas with KOH a feebly laevorotatory product containing much (II) and little (III) is obtained. Treatment of (I) with SOCl₂ at room temp. leads to the ester $\text{SO} \left\langle \begin{array}{l} \text{O} \cdot \text{CH} \cdot \text{CO}_2 \text{Et} \\ \text{O} \cdot \text{CH} \cdot \text{CO}_2 \text{Et} \end{array} \right.$ b.p. 166°/9 mm., hydrolysed by acidified H₂O exclusively to (II) and by KOH mainly to (II) accompanied by (III). Hydrolysis of the corresponding ester of (IV) yields almost exclusively (IV). Et mesodichlorosuccinate is converted by Ag₂O entirely into (II), by KOH into (II) accompanied by a little (III). Et *l*-isodichlorosuccinate and KOH yield (IV) with a small proportion of (III). *l*-isoDichlorosuccinic acid and Ag₂O give small amounts of *l*-tartaric acid. H. W.

Beryllium tartrate.—See this vol., 732.

Steric series. XIX. Configuration of the tertiary carbon atom. II. α -Hydroxy- α -methylfatty acids. K. FREUDENBERG, W. F. BRUCE, and E. GAUF (Annalen, 1934, 510, 206—222; cf. A., 1933, 502).—(—)- $\alpha\alpha'$ -Dihydroxyadipic acid has the optical properties of a *d*-hydroxyacid and is assigned the constitution (I, R=H), whilst *d*-(—)- $\alpha\alpha'$ -dihydroxy- $\alpha\alpha'$ -dimethyladipic acid is (I, R=Me). The racemoid form of $\alpha\alpha'$ -dihydroxy- α -methyladipic acid must be (II), since it gives a dilactone; the configurations of the *d*-(—) and *l*-(+)-forms are deduced from the rotatory powers of the components *A* and *B*.



When freshly distilled laevulaldehyde (III) (prep. by ozonolysis of caoutchouc and subsequent reductive fission described) is kept at 0°, it polymerises to the trimeride, $\text{O} \left\langle \begin{array}{l} \text{CHR} \cdot \text{O} \\ \text{CHR} \cdot \text{O} \end{array} \right\rangle \text{CHR}$ (R=CH₂·CH₂·COMe), m.p. 78—79° (trioxime, m.p. 139—149°); polymerisation is retarded by dilution with H₂O or abs. Et₂O. The nitrile from (III), aq. KCN, and conc. HCl in the cold is hydrolysed (cold conc. HCl-Et₂O) to mesoid $\alpha\alpha'$ -dihydroxy- α -methyladipic acid, m.p. 177—178°, and racemoid $\alpha\alpha'$ -dihydroxy- α -methyladipic acid (II), m.p. 164—165° [dilactone, b.p. 154—155°/11—12 mm., m.p. 75—76°; Ac₂ derivative, m.p. 157.5—158°; di(phenylhydrazide), m.p. 216°; diamide, m.p. 141°]. (II) is resolved by brucine into the (+)-form, m.p. 173—174° (decomp.), [α]₅₇₈ +13.8±0.1° in H₂O, -7.8° as K₂ salt [dilactone, m.p. 110—111°, [α]₅₇₈ +27.5±0.3° in salt; Me₂ ester, [α]₅₇₈ +9.7° in MeOH; di(phenylhydrazide), m.p. 227—228°, [α]₅₇₈ -19.7° in C₅H₅N; diamide, m.p. 155—155.5°, [α]₅₇₈ -36.5°; Ac₂ derivative, m.p. 142—143°, [α]₅₇₈ -13.1° in MeOH]. Acetylacetone and HCN similarly give (cf. Fittig, A., 1907, i, 471) meso-, m.p. 210°, and *r*- (IV), m.p. 210°, $\alpha\alpha'$ -dihydroxy- $\alpha\alpha'$ -dimethyladipic acids; (IV) is isol-

ated and purified through its dilactone. Resolution of (IV) with cinchonidine affords the (—)-form, [α]₅₇₈ -17° in H₂O, -0.5±0.2° as K₂ salt [dilactone, m.p. 110—111°, [α]₅₇₈ -38.2° in dioxan; Me₂ ester, m.p. 49—50°, [α]₅₇₈ -18.4° in MeOH; Ac₂ derivative, m.p. 101°, [α]₅₇₈ +17.8° in MeOH; di(phenylhydrazide), m.p. 234° (decomp.), [α]₅₇₈ +26° in C₅H₅N; diamide, m.p. 219—220°, [α]₅₇₈ +19.8° in H₂O]. *l*-(+)- $\alpha\alpha'$ -Dihydroxyadipic acid, [α]₅₇₈ +4.2° in H₂O, -30.3° as Na₂ salt [dilactone, m.p. 120—121°, [α]₅₇₈ +11.2° in dioxan; Me₂ ester, [α] < -0.5°; Ac₂ derivative, m.p. 159° (decomp.), [α]₅₇₈ -28.5° in MeOH; diamide, m.p. 164°, [α]₅₇₈ -64.6° in H₂O; di(phenylhydrazide), m.p. 191°, [α]₅₇₈ -15.8° in C₅H₅N], is prepared by a modification of Le Sueur's method (J.C.S., 1908, 93, 718). H. B.

Unsaturated polycarboxylic acids. Derivatives of ethylenetricarboxylic acid. (MLLE.) T. GRADOWSKA, A. KRYNICKI, and R. MATACHOWSKI (Bull. Acad. Polonaise, 1933, A, 552—559).—With Br in CCl₄ Me ethane- $\alpha\alpha\beta$ -tricarboxylate affords its α -Br-derivative, b.p. 148.5—149.5°/9 mm., converted by NaOMe-MeOH into the α -OMe-ester, b.p. 142—143°/7 mm. (Et α -ethoxy-ester, b.p. 158—160°/11 mm.), and by C₅H₅N into Me ethylenetricarboxylate (I), b.p. 128—134°/8 mm., m.p. 40—41° (Et ester, b.p. 155—156°/11 mm.). (I) readily forms additive compounds and hydrolysis with cold 4% aq. Ba(OH)₂ gives the Ba salt of an acid +H₂O, m.p. 145—146°, which does not regenerate (I) with CH₂N₂. Addition of H₂O, NH₂Ph, or NH₃ to (I) affords, respectively, Me β -hydroxy- (Et ester, b.p. 158—160°/11 mm. with slight decomp.) and β -anilino-, m.p. 82°, ethane- $\alpha\alpha\beta$ -tricarboxylate, and di-($\alpha\beta\beta$ -tricarboxymethoxyethyl)amine, m.p. 122°. J. W. B.

Properties of citric acid. S. BERLINGOZZI (Annali Chim. Appl., 1934, 24, 217—224).—The heating curve of citric acid (+H₂O) shows a point of inflexion at about 56°, at which temp. the anhyd. acid (free from aconitic acid) is formed. Fusion occurs at about 70—100° and decomp. at 140°. To detect aconitic in citric acid (1 : 10,000 or more), 10 g. of the powdered acid are well shaken with about 20 c.c. of H₂O-free Et₂O, this being filtered and the residue washed with a little Et₂O. The filtrate is evaporated, the residue dissolved in H₂O, and the solution made faintly alkaline with dil. NaOH, cooled, and treated with 2—3 drops of 2% KMnO₄; a green colour shows aconitic (or itaconic, mesaconic, or citraconic) acid. T. H. P.

Resolution of *dl*-erythronic acid. J. W. E. GLATTFELD and L. R. FORBRICH (J. Amer. Chem. Soc., 1934, 56, 1209—1210).—*dl*-Erythronolactone, m.p. 91—92°, prepared by oxidation (AgClO₃; Braun, A., 1929, 293) of γ -hydroxyisocrotonolactone (A., 1931, 1148), is resolved by brucine and quinine into *d*-(—), m.p. 105° (corr.), [α]₅₄₆ -87.62°, and *l*-(+)-, m.p. 105° (corr.), [α]₅₄₆ +87.32°, -forms. H. B.

Convenient modification of the Kiliani synthesis of higher carbon acids (or their lactones) from reducing sugars. C. S. HUDSON, O. HARTLEY, and C. B. PURVES (J. Amer. Chem. Soc., 1934, 56, 1248—1249).—Glucose (3 mols.) is treated with NaCN (3.3 mols.) and CaCl₂ (3.6 equivs.) in H₂O at

room temp. for 22 hr.; $\text{Ca}(\text{OH})_2$ (3 mols.) is then dissolved in the solution. The basic Ca salts which subsequently separate are washed with cold aq. $\text{Ca}(\text{OH})_2$ and then decomposed with $\text{H}_2\text{C}_2\text{O}_4$ or H_2SO_4 . α -Glucoheptonolactone is thus obtained in 58% yield; the β -lactone (21%) is obtained through the brucine salt. The method has been applied to xylose and lactose; the gluco-octonolactones have been prepared.

H. B.

Thio- and thionyl-difatty acids. E. LARSSON and K. JÖNSSON (Ber., 1934, 67, [B], 757—760).—Conc. solutions of $\text{SK}\cdot\text{CMe}_2\cdot\text{CO}_2\text{K}$ and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$ in H_2O at 100° yield $\alpha\alpha$ -dimethylthiodiacetic acid, m.p. 111° , oxidised by 30% H_2O_2 in COMe_2 at room temp. to $\alpha\alpha$ -dimethylthionylthiodiacetic acid, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{SO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m.p. 114° . Trimethylthiodiacetic acid, m.p. 111° , from $\text{SH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ and $\text{CHBrMe}\cdot\text{CO}_2\text{H}$ or from $\text{SH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ and $\text{CBrMe}_2\cdot\text{CO}_2\text{Et}$, followed by hydrolysis, is converted by H_2O_2 in AcOH at 0° into trimethylthionylthiodiacetic acid, m.p. 87° . Thioacetic- β -propionic acid, m.p. 94° , from $\text{SH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ or from $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and $\text{CH}_2\text{I}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, with H_2O_2 in COMe_2 gives thionylacetic- β -propionic acid, m.p. 90° (decomp.). Thio- β -propionic- α -isobutyric acid, m.p. 106° (from $\text{SH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and $\text{CBrMe}_2\cdot\text{CO}_2\text{Et}$), or m.p. 109° (from $\text{SH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ and $\text{CH}_2\text{I}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$), is oxidised by H_2O_2 to the non-cryst. (?) thionyl acid and by $\text{Br}\cdot\text{H}_2\text{O}$ to sulphonyl- β -propionic- α -isobutyric acid, m.p. 156° .

H. W.

Sulphoglutaric acid. J. M. VAN DER ZANDEN (Rec. trav. chim., 1934, [iv], 53, 591—597).—Glutaconic acid (modified prep.) and $(\text{NH}_4)_2\text{SO}_3$ at 100° give β -sulphoglutaric acid, $+\text{H}_2\text{O}$, m.p. 109 — 111° (Ba, $\text{Pb}_{1.5}$, K_2 , K , and Tl_3 salts) (could not be obtained pure from β -bromoglutaric acid), which with H_2SO_4 gives probably impure trisulphoglutaric acid (Ba₂ salt), whilst the Et H ester gives mixtures.

R. S. C.

Formation of formaldehyde in the oxidation of ethyl alcohol. M. FLANZY (Compt. rend., 1934, 198, 1793—1795).— CH_2O (I) is formed in the oxidation of EtOH with $\text{MnO}_2 + \text{H}_3\text{PO}_4$ or H_2SO_4 at 100° , H_2O_2 in conc. aq. NH_3 [increased by Cu; larger amounts of (I) from NH_2Et and EtI ; HCO_2H in alkaline media free from NH_3], $\text{K}_2\text{Cr}_2\text{O}_7\text{--H}_2\text{SO}_4$ at 100° (greater if the concn. of active O is $>$ that of EtOH), but not if oxidation is begun in the cold and the temp. then raised to 100° . The formation of (I) may be due to intermediate production of $\text{CH}_2\cdot\text{CH}_2\text{OH}$.

J. W. B.

Chains in the acetaldehyde decomposition. D. V. SICKMAN and A. O. ALLEN (J. Amer. Chem. Soc., 1934, 56, 1251).— MeCHO (I) decomposes completely at 300° in presence of a few % of azomethane (II), indicating the existence of a chain decomp. which is initiated by free Me radicals. Chain lengths (calc. from rate measurements) are about 30. The rate \propto to the pressure (p) of (I) and \sqrt{p} of (II), as predicted by the chain theory.

H. B.

Extension of the Cannizzaro reaction to aliphatic and arylaliphatic aldehydes. S. SABETAY and L. PALFRAY (Compt. rend., 1934, 198, 1513—1515; cf. A., 1932, 867).—0.5—1.5 g. of an aliphatic

or arylaliphatic aldehyde with 25 c.c. of boiling 0.5N- $\text{CH}_2\text{Ph}\cdot\text{OK}$ during 2—5 hr. often affords the corresponding acid and alcohol quantitatively. J. L. D.

Detection of the simplest hydroxy-aldehydes and ketones by means of colour reactions. E. TOMMILA (Suomen. Kem., 1934, 7, 85—86B).—Characteristic coloured ppts. and solutions in Et_2O (I) are obtained by treating OH-aldehydes with naphthoresorcinol in conc. HCl . The following are described, the sensitivity being given in parentheses: $\text{OH}\cdot\text{CH}_2\cdot\text{CHO}$ (II), greyish-green ppt., insol. in CHCl_3 (III), bluish-green, fluorescent solutions (10^{-5} g.); AcCHO , red ppt. and red solutions in (I), (III), and NaOH with powerful blue fluorescence (5×10^{-6} g.); glyceraldehyde, greyish-blue ppt., insol. in (III), yellow, non-fluorescent solution (10^{-5} g.); dihydroxyacetone, greyish-violet ppt., yellow—pale violet, non-fluorescent solution [colourless in (III)], transient violet with NH_3 ; tetrose from (II), bright red insol. ppt. Similar, less characteristic reactions are described with resorcinol, orcinol, and phloroglucinol.

S. C.

Catalytic reduction reactions. K. PACKENDORFF (Ber., 1934, 67, [B], 905—908).—An active catalyst is obtained by reducing H_2PtCl_6 by H_2 in presence of Pt-C. It is particularly suitable for operation in HCl , whereas HNO_3 is reduced to NH_3 and the reduction products of H_2SO_4 restrict its activity. The optimal concn. of HCl varies from case to case, but if > 10 — 12% the activity is restricted. In alkaline solution absorption of H is slower than in acid medium. Ketones not belonging to the type COPhMe are reduced to the carbinols generally accompanied by the hydrocarbons. The following examples are cited: COEt_2 to $\text{CHEt}_2\cdot\text{OH}$; $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$ to $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$; acetyl-cyclohexane to methylcyclohexylcarbinol; laevulic acid to valerolactone and valeric acid; phthalimide to phthalimidine; cyclohexanone to cyclohexanol and cyclohexane, and cyclopentanone to cyclopentanol and cyclopentane, whereby reaction ceases before production of hydrocarbon is complete even when the amount of catalyst is greatly increased; citral ($+2\text{H}$) to unchanged material, geraniol+citronellol, and hydrocarbon.

H. W.

Action of sodium on aliphatic ketones. (Existence of metal ketyls in the acyclic series.) A. E. FAVORSKI and I. N. NAZAROV (Bull. Soc. chim., 1934, [v], 1, 46—65).—The dimeride of the Na derivative of $\beta\beta\delta\delta$ -tetramethylpentan- γ -one [which with CO_2 in Et_2O in absence of O_2 gives $\alpha\alpha$ -ditert.-butylglycollic acid, an oil (*Ag* salt)] is converted by acid into $\beta\beta\delta\delta$ -tetramethylpentan- γ -ol and tetratert.-butylethylene glycol (I), m.p. 85 — 86° , which with conc. H_2SO_4 at -16° affords $\beta\beta$ -dimethyl- $\delta\delta\delta$ -tritert.-butylbutan- γ -one, b.p. 135 — $136^\circ/20$ mm. [Br_2 -derivative, m.p. 74 — 75° (decomp.)]. The dimeride of the Na derivative of $\beta\delta\delta$ -trimethylpentan- γ -one (II) is decomposed by H_2O into (II) and the corresponding tert.-alcohol, together with $\beta\epsilon$ -dimethyl- $\gamma\delta$ -ditert.-butylhexane- $\gamma\delta$ -diol, b.p. 133° . The Na derivative of pinacolin (III) when heated in a sealed tube at 110° for 15—20 hr. gives an alcohol, $\beta\beta\delta\delta\epsilon\epsilon$ -hexamethylhexan- γ -one (IV), b.p. 90 — $91^\circ/15$ mm. [reduced ($\text{Na}\cdot\text{EtOH}$) to an

alcohol, b.p. 99°/15 mm. (*Bz* derivative, m.p. 48—49°), which is oxidised (KMnO_4) to (III), $\text{Bu}^{\gamma}\text{CO}_2\text{H}$ (V), and $\text{COBu}^{\gamma}\text{CO}_2\text{H}$ (VI)], and $\beta\gamma$ -ditert.-butyl- Δ^{α} -butan- γ -ol (VII), b.p. 105—107°/15 mm. (Br-compound, an oil), oxidised (KMnO_4) to (III), (V), and (VI), and converted by distillation with anhyd. $\text{H}_2\text{C}_2\text{O}_4$ into $\beta\gamma$ -ditert.-butylbutadiene (VIII), b.p. 62—64°/15 mm. (Br_2 -compound, an oil), and (III). Interaction of (VIII) with maleic anhydride in C_6H_6 in a sealed tube at 100° during 3 hr. affords $\beta\gamma$ -ditert.-butyltetrahydrophthalic anhydride, m.p. 128—129°, hydrolysed to the acid, m.p. 183—184° (decomp.) (*Ag* salt). J. L. D.

Condensation of alkylacetylenes with hydroxy-compounds. G. F. HENNING and D. B. KILLIAN [with T. H. VAUGHN and J. A. NIEUWLAND] (*J. Amer. Chem. Soc.*, 1934, 56, 1130—1132).— $\text{CH}_2\text{C}\equiv\text{CBu}$ and MeOH in presence of BF_3 (prep.: A., 1933, 932) and HgO give the *Me*₂ acetal, b.p. 58—60°/30 mm., of COMeBu . Δ^{α} -Heptinone and $(\text{CH}_2\text{OH})_2$ similarly afford the acetal, $\begin{matrix} \text{CH}_2\text{O} \\ \text{CH}_2\text{O} \end{matrix} > \text{CMe}\cdot\text{C}_5\text{H}_{11}$, b.p. 180—181°/745 mm.; with AcOH , α -amylvinyl acetate (I), b.p. 92—94°/40 mm., and a little *Me* amyl ketone (II) result. (I) is hydrolysed (20% EtOH-KOH) to (II); ammonolysis of (I) gives (II) and NH_2Ac . (I) is stable to dil. acid or alkali. H. B.

Action of magnesium ethyl bromide on sebactetramethyldiamide. (MLLE.) V. PARASKOVA (*Compt. rend.*, 1934, 198, 1701—1703; cf. A., 1928, 50).—Interaction of sebactetramethyldiamide (I) with excess of MgEtI in boiling Et_2O during many hr. affords tetradecane- $\gamma\mu$ -dione, m.p. 78° (*disemicarbazone*, m.p. 186—187°; *dioxime*, m.p. 105—106°), *i*-ketododecodiethylamide, b.p. 216—218°/15 mm., hydrolysed to the acid, m.p. 72° (*semicarbazone*, m.p. 169°; *Et* ester, b.p. 175—176°/13 mm., and its *semicarbazone*, m.p. 81—82°); μ -diethylamino- μ -ethyltetradecan- γ -one, b.p. 209—212°/12 mm. (*semicarbazone*, m.p. 98—99°) (converted by boiling Ac_2O into a product, free from N, b.p. 173—174°/16 mm.), $\gamma\mu$ -di-(diethylamino)- $\gamma\mu$ -diethyltetradecane and *i*-diethylamino-*i*-ethyl-dodecodiethylamide, oils, which lose N with boiling Ac_2O . (I) probably reacts through its enolic form (cf. A., 1931, 831). J. L. D.

Polarity and alcoholysis of $\alpha\gamma$ -diketones and β -keto-esters. L. J. BECKHAM and H. ADKINS (*J. Amer. Chem. Soc.*, 1934, 56, 1119—1123).—Mechanisms for the alcoholysis of $\alpha\gamma$ -diketones and β -CO-esters in acid and alkaline solutions are formulated and the influence of the polarity ($\pm I$; $\pm T$) of substituent groups considered. Predictions are in accordance with the results previously obtained (A., 1930, 1273, 1559; 1931, 69; 1932, 1020, 1112). H. B.

Preparation of *l*-ribose. W. C. AUSTIN and F. L. HUMOLLER (*J. Amer. Chem. Soc.*, 1934, 56, 1152—1153).—Acetobromo-*l*-arabinose is reduced ($\text{Zn} + 5\% \text{ Zn-Cu}$, AcOH) to *l*-arabinal diacetate. Oxidation of *l*-arabinal in H_2O with BzO_2H in EtOAc at $< 8^\circ$ gives (cf. A., 1933, 147) 40% of *l*-ribose, m.p. 85—87°, $[\alpha]_D^{25} = +22.6^\circ$ in H_2O (*p*-bromophenylhydrazone, m.p. 170—172°), and 8% of *l*-arabinose (*p*-bromophenylhydrazone, m.p. 161—162°). H. B.

Preparation of β -*d*-allose. F. P. PHELPS and F. BATES (*J. Amer. Chem. Soc.*, 1934, 56, 1250; cf. Levene and Jacobs, A., 1911, i, 14).—*d*-Ribose (from yeast-nucleic acid) is converted (cf. *loc. cit.*) into *d*-altronic acid (as *Ca* salt) and *d*-allonolactone (I). Reduction (Na-Hg) of (I) gives β -*d*-allose, m.p. 128—128.5°, $[\alpha]_D^{20} = +0.58^\circ$ (after 2 min.) $\rightarrow +14.41^\circ$ (const.). H. B.

Preparation of two new crystalline aldohexoses, *l*-allose and *l*-altrose, from *l*-ribose by the cyanohydrin reaction. W. C. AUSTIN and F. L. HUMOLLER (*J. Amer. Chem. Soc.*, 1934, 56, 1153—1155).—*l*-Ribose is treated with aq. $\text{Ca}(\text{CN})_2$ at 10° until the solution shows no reducing power; successive treatment with $\text{Ba}(\text{OH})_2$, $\text{H}_2\text{C}_2\text{O}_4$, and $\text{Ca}(\text{OH})_2$ and concn. of the resulting solution gives *Ca l*-altronate ($+3.5\text{H}_2\text{O}$). Removal of *Ca* from the residual solution with $\text{H}_2\text{C}_2\text{O}_4$ and evaporation give *l*-allonolactone (I), m.p. 130°, $[\alpha]_D +6.32^\circ \rightarrow +4.34^\circ$. Reduction (Na-Hg , dil. H_2SO_4) of (I) affords *l*-allose, m.p. 128—129°, $[\alpha]_D -1.9^\circ \rightarrow -13.88^\circ$ (cf. A., 1933, 699) (*phenylosazone*, m.p. 165°; *p*-bromophenylhydrazone, m.p. 141—145°). *l*-Altronolactone, $[\alpha]_D -37.2^\circ$, is similarly reduced to *l*-altrose, m.p. 107—109.5°, $[\alpha]_D -28.75^\circ \rightarrow -32.3^\circ$ (*phenylosazone*, m.p. 165°; *phenylbenzylhydrazone*, m.p. 147—148°). Brucine *l*-allonate, m.p. 168—169°, $[\alpha]_D -24.75^\circ$, and *l*-altronate, m.p. 171—175°, $[\alpha]_D -21.44^\circ$, and *l*-allonphenylhydrazide, m.p. 151—155°, are described. All rotations are in H_2O at 20—25°. H. B.

Structure and properties of acetone-methyl-rhamnopyranoside. P. A. LEVENE and I. E. MUSKAT (*J. Biol. Chem.*, 1934, 105, 431—442).—2:3-isoPropylidinemethylrhamnopyranoside ($\alpha + \beta$), b.p. 110—112°/1 mm., $[\alpha]_D^{25} -14.1^\circ$ in H_2O , is converted by MeI and Ag_2O or MeI and K in liquid NH_3 into a 4-*Me* derivative, b.p. 67—68°/0.3 mm., $[\alpha]_D^{25} -24^\circ$ in H_2O (*p*-toluenesulphonate, m.p. 58°, $[\alpha]_D^{25} +14^\circ$ in MeOH ; unaffected by NaI in COMe_2 at 100°), which is hydrolysed by dil. H_2SO_4 at 100° to 4-methylrhamnopyranose, m.p. 122°, $[\alpha]_D^{25} +12.9^\circ$ in MeOH [purified through its Ac_3 derivative (I), b.p. 114—116°/0.17 mm., $[\alpha]_D^{25} -12.2^\circ$ in MeOH ; *phenylhydrazone*, decomp. 176°], the structure of which is determined by oxidation with aq. Ag_2O to β -hydroxy- α -methoxy-*n*-butyric acid (*Ag* salt). With HBr in AcOH (I) gives bromomethylrhamnopyranose diacetate, m.p. 140.5°, $[\alpha]_D^{25} -178.6^\circ$ in CHCl_3 , which with Ag_2O and MeOH gives methylmethylrhamnopyranoside diacetate, b.p. 125—130°/0.7 mm., $[\alpha]_D^{25} +17.2^\circ$ in MeOH , and with Ag theophylline in xylene at 100° gives methyltheophyllinerhamnopyranoside diacetate, $[\alpha]_D^{25} -36.7^\circ$ in MeOH , and finally with MeOH and a little quinoline affords evidence of the formation of an orthoacetate not isolated pure. H. A. P.

New acetone [isopropylidene] sugar. R. WEIDENHAGEN (*Z. Ver. deut. Zuckerind.*, 1934, 84, 335—340).—Gradual addition of dry Ag_2CO_3 to acetobromoglucose in anhyd. COMe_2 containing ignited K_2CO_3 at about 5° causes vigorous evolution of CO_2 . After removal of solvent, the residue is dissolved in C_6H_6 and the solution is washed with H_2O at 25—28° until reducing substances of the trehalose type are removed. When preserved the

C_6H_6 solution deposits *isopropylidenedi-1:1-glucose octa-acetate* (I), m.p. 154.5—156° (corr.), $[\alpha]_D^{20} -31.1^\circ$ in C_6H_6 , hydrolysed by NaOMe in MeOH to non-cryst. *isopropylidenedi-1:1-glucose*, from which (I) is regenerated by Ac_2O in C_5H_5N . H. W.

Ring opening of galactose acetates. J. COMPTON and M. L. WOLFROM (J. Amer. Chem. Soc., 1934, 56, 1157—1162).— β -Galactopyranose tetra-acetate (I), m.p. 112° [127—128° in alkali-free glass (cf. Georg, A., 1932, 835)], from acetobromogalactose (Unna, Diss., Berlin, 1911), and $NPhMe \cdot NH_2$ (II) in dil. AcOH give aldehydogalactosephenylmethylhydrazone 2:3:4:6-tetra-acetate, m.p. 122—123°, $[\alpha]_D^{20}$ (in C_5H_5N) $-12^\circ \rightarrow +37.5^\circ$, acetylated (Ac_2O , C_5H_5N) to the penta-acetate (III) (A., 1931, 1276), and converted by *p*- $C_6H_4Me \cdot SO_2Cl$ in C_5H_5N into aldehydogalactosephenylmethylhydrazone 2:3:4:6-tetra-acetate 5-*p*-toluenesulphonate, m.p. 143—144°, $[\alpha]_D^{20} +21.4^\circ$ in C_5H_5N . (I) and $NHPh \cdot NH_2$ (IV) in dil. AcOH give aldehydogalactosephenylhydrazone 2:3:4:6-tetra-acetate, $[\alpha]_D^{20} +5^\circ$ in C_5H_5N , acetylated to the corresponding penta-acetate (V) (*loc. cit.*). β -Galactofuranose tetra-acetate (VI) (improved prep. given; cf. Hudson and Johnson, A., 1916, i, 546) and (II) similarly afford aldehydogalactosephenylmethylhydrazone 2:3:5:6-tetra-acetate, m.p. 126°, $[\alpha]_D^{20} +59.1^\circ$ in C_5H_5N (4-*p*-toluenesulphonate, m.p. 102—103°, $[\alpha]_D^{20} +60.7^\circ$ in C_5H_5N), also acetylated to (III). (VI) and (IV) give aldehydogalactosephenylhydrazone 2:3:5:6-tetra-acetate, m.p. 139—140°, $[\alpha]_D^{20} +80.1^\circ$ in C_5H_5N , acetylated further to (V). The reactions of aldehydogalactose penta-acetate, (I), and (VI) with (II) and (IV) at 0° are all unimol.; reaction is about 45 times as rapid with (VI) as with (I). H. B.

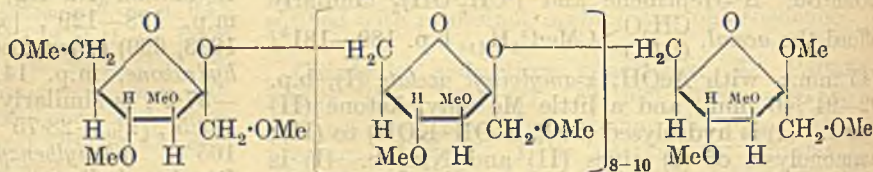
Carbohydrates. XIX. Synthetic derivatives of fructofuranose. P. BRIGL and R. SCHINLE (Ber., 1934, 67, [B], 754—757; cf. this vol., 173).—Fructofuranose tetrabenzoate is converted by Ag_2O and MeI into methylfructofuranoside tetrabenzoate, $[\alpha]_D^{20} +5.0^\circ$ in $CHCl_3$, hydrolysed by $Ba(OH)_2 \cdot 8H_2O$ in MeOH at 15—20° to α -methylfructofuranoside (I), $[\alpha]_D^{20} +48.8^\circ$ in H_2O , $+42.4^\circ$ in EtOH, isolated by filtration of $Ba(OBz)_2$, evaporation of the filtrate in vac., and extraction of the residue with $COMe_2$. (I) is transformed by Me_2SO_4 and NaOH into tetramethylmethylfructofuranoside, b.p. 100—102°/0.6 mm., $[\alpha]_D^{20} +77.6^\circ$ in H_2O , the furanose structure of which is confirmed by the val. $[\alpha]_D^{20} +22.6^\circ$ of the product of its hydrolysis by 1% HCl. H. W.

Acetylation of sorbose in presence of pyridine. G. ARRAGON (Compt. rend., 1934, 198, 1503—1510; c. A., 1933, 811).—Sorbose in Ac_2O containing C_5H_5N at 0° affords the tetra-acetate (50%), m.p. 101.5°, $[\alpha]_{578}^{20} -22^\circ 35'$, whereas that formed in presence of $ZnCl_2$ has m.p. 96.5°, $[\alpha]_{578}^{20} -21^\circ 30'$ in $CHCl_3$. At room temp. some penta-acetate is formed.

J. L. D.

Polysaccharides. XVII. Constitution and chain-length of levan. S. W. CHALLINOR, W. N.

HAWORTH, and E. L. HIRST (J.C.S., 1934, 676—679).—Levan, $[\alpha]_D^{20} -47^\circ$ in H_2O , prepared (cf. Harrison *et al.*, A., 1931, 267) from sucrose by the action of *B. mesentericus*, is hydrolysed (0.5% aq. $H_2C_2O_4$) to fructose and methylated (method: Hibbert *et al.*, *ibid.*, 827) to trimethyl-levan (I), $[\alpha]_D^{20} -60^\circ$ in $CHCl_3$. The fractions obtained by successive additions of light petroleum to a solution of (I) in $CHCl_3 \cdot COMe_2$ (1:1) are (apart from the first which contains all the mineral impurities) similar ($[\alpha]$; η_{sp} ; OMe; the m.p. varies somewhat), indicating that (I) is homogeneous. Hydrolysis (aq. MeOH— $H_2C_2O_4$ at 80°) of the various fractions and subsequent treatment with MeOH—HCl gives 1:3:4:6-tetra-methyl- (10—11%) (II) and 1:3:4-trimethyl-methylfructofuranoside (III). (II) is converted (A., 1927, 1057) into 2:3:4:6-tetramethylfructuronamide, whilst (III) is hydrolysed to 1:3:4-trimethylfructose, m.p. 75°. These results indicate that (I) has the following structure.



The I no. of levan indicates an apparent mol. wt. of 3800. Viscosity measurements with (I) indicate a chain-length which is about twice that determined chemically. H. B.

Glucoside of *Coronilla* seeds.—See this vol., 709.

Highly polymerised compounds. LXXXXII. Constitution of cellulose. H. STAUDINGER (Cellulosechem., 1934, 15, 53—59, 65—67).—The author's views are stated at length. Measurements of the viscosity of cellulose (I) in Schweitzer's reagent (II) can be applied to the determination of (I) if a large excess of Cu salts and NH_3 is used and observations are made in absence of light and air. (I) has a degree of polymerisation of about 750. Technical (I) is less highly polymerised, since marked degradation occurs during the removal of lignin. The very high viscosity of cellulose nitrate is explained by the hypothesis that native (I) consists of very complex esters which are hydrolysed by (II) or by mercerisation. After the alkaline treatment (I) and the nitrate (III) derived from it have the same mol. structure and the viscosity of (I) in (II) is the same as that of (III) in BuOAc. Nitration of native (I) is not accompanied by rupture of ether or ester linkings, and hence a very viscous nitrate results. H. W.

Precautions necessary in measuring the mol. wt. of cellulose derivatives. M. MATHIEU (Chim. et Ind., 1934, 31, Spec. No., 792—796).—For correct determinations of mol. wt. by measurements of η or osmotic pressure it is essential that the mols. be completely dispersed. Evidence on this point for cellulose nitrate may be obtained by the X-ray examination of films dried on H_2SO_4 at room temp. A. G.

Mol. wts. of celluloses. E. O. KRAEMER and W. D. LANSING (Nature, 1934, 133, 870—871).—Mol. wts. of cellulose determined by sedimentation

equilibrium range from 60,000 to 180,000, and the estimated mol. wt. of native cellulose is near 300,000.

L. S. T.

Asymmetric nitrogen atom. LIX. Decomposition of quaternary ammonium nitrates under the influence of amines; rate of decomposition as function of the basicity of amines. E. WEDEKIND and F. FEISTEL (Ber., 1934, 67, [B], 845—853; cf. A., 1931, 75).—The rate of reaction of quaternary ammonium nitrates with amines, $\text{NR}'\text{R}''\text{R}'''\text{R}''''\text{NO}_3 + \text{HNXY} \rightleftharpoons \text{NR}'\text{R}''\text{R}'''+ + \text{NR}''''\text{XY} + \text{HNO}_3$ has been determined generally by measurements of electrical conductivity, less frequently polarimetrically. *tert.*-Bases ($\text{C}_5\text{H}_5\text{N}$, quinoline, NPhMe_2 , NEt_3 , NPhMeEt , dimethylaminoantipyrine) are inactive. The relationship between the strength of the base and its effect is very pronounced. β - is more powerful than α - $\text{C}_{10}\text{H}_7\text{-NH}_2$. For $\text{C}_6\text{H}_4\text{Me-NH}_2$ and $\text{C}_6\text{H}_4\text{Cl-NH}_2$ basicity and effect diminish in the sequence *p*-, *m*-, *o*-, which holds also for $\text{C}_6\text{H}_4(\text{NH}_2)_2$. NH_2Ph is somewhat weaker than *o*- $\text{C}_6\text{H}_4\text{Me-NH}_2$. The half-val. periods for NHEt_2 , $\text{NHEt-CH}_2\text{Ph}$, and $\text{NH}(\text{CH}_2\text{Ph})_2$ are in the ratio, 26 : 40 : 80. A similar increase in effect is observed in the sequence NH_2Ph , NPhEt , NPhMe . The action of tetrahydro-isoquinoline is about three times as great as that of -quinoline. The inactivity of $\text{NO}_2\text{-C}_6\text{H}_4\text{-NH}_2$, *p*- $\text{OH-C}_6\text{H}_4\text{-NH}_2$, *p*- $\text{NH}_2\text{-C}_6\text{H}_4\text{-CO}_2\text{H}$, and NPh_2 is in harmony with the slight basicity. $\text{p-C}_6\text{H}_4(\text{NH}_2)_2$ is more active than $[\text{C}_6\text{H}_4\text{-NH}_2]_2$ which greatly excels NH_2Ph , whereas $[\text{NPh}]_2$ is inactive. Modifications of the apparatus necessitated by the high resistances are described. H. W.

Preparation of hexamethylenetetramine. C. L. TSENG and M. HU (Sci. Quart. Nat. Univ. Peking, 1934, 4, 243—249).— $(\text{CH}_2)_6\text{N}_4$ has m.p. 293—295° (lit. 263°, 230.4°). W. R. B.

Proteolytic enzymes. III, IV. Synthesis of peptides etc. See this vol., 809.

Synthetic sugar-amino-acid compounds. M. BERGMANN, L. ZERVAS, and J. OVERHOFF (Z. physiol. Chem., 1934, 224, 52—55).—The Na compound of benzylideneglucose (I) with carbobenzyloxyglycyl chloride (II) affords 1-(carbobenzyloxyglycyl)-4 : 6-benzylideneglucose, m.p. 180° (corr.), which on hydrogenation gives 1-glycyl-d-glucose [sulphate, sinters > 110° (decomp.), $[\alpha]_D^{20} + 12.8^\circ$ in H_2O . In presence of $\text{C}_5\text{H}_5\text{N}$, (I) and (II) yield 1 : 2 : 3-tri(carbobenzyloxyglycyl)-4 : 6-benzylideneglucose, m.p. 96°, which on hydrogenation gives 1 : 2 : 3-triglycyl-d-glucose (sulphate). J. H. B.

Stability of cystine in acid solution. K. SHINOHARA and M. KILPATRICK (J. Biol. Chem., 1934, 105, 241—251).—Cystine (I) is produced when cystine (II) in HCl is kept even in an atm. of N_2 in the dark at room temp., the change becoming detectable (by I titration) after an induction period of 7 days. Formation of (I) is much more rapid at 80°, or in alkaline solution, and is not affected by Cu^{++} or Fe^{+++} . A modified nitroprusside test for the determination of SH compounds, and a colorimetric method for the determination of (I) in presence of (II) based on the reaction between (I) and CoCl_2 and alkaline H_2O_2 ,

are described. (I) can be qualitatively differentiated from other similar compounds by means of the complex Co test. A. E. O.

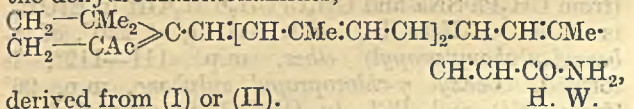
Biuret reaction. IV. (a) Biuret salt of triglycylglycine. (b) Biuret salt of glycine anhydride. (c) Barium biuret salt of succinimide. M. M. RISING, F. M. PARKER, and D. R. GASTON (J. Amer. Chem. Soc., 1934, 56, 1178—1180; cf. A., 1933, 382).—Triglycylglycine and $\text{Cu}(\text{OH})_2$ in aq. NaOH give *Na Cu triglycylglycine*, $\text{Na}_2\text{CuC}_8\text{H}_{10}\text{O}_5\text{N}_4 \cdot 2\text{H}_2\text{O}$, m.p. 280° (decomp.; corr.) (chars at 278°). The unstable *Na Cu glycine anhydride*, $\text{Na}_2\text{CuC}_8\text{H}_8\text{O}_4\text{N}_4 \cdot 4\text{H}_2\text{O}$, decomp. > 120°, is similarly prepared. *Ba Cu succinimide*, $\text{BaCuC}_{16}\text{H}_{16}\text{O}_8\text{N}_4$, m.p. 257° (decomp.; corr.), is obtained from succinimide, $\text{Cu}(\text{OAc})_2$, and $\text{Ba}(\text{OH})_2$ in aq. EtOH. Structures are suggested. The view (A., 1931, 77) that four basic N atoms are involved in the biuret reaction is supported. H. B.

Catalytic preparation of nitriles from esters in presence of Japanese acid clay. J. ABE (Bull. Waseda Appl. Chem. Soc., 1933, 21, 27—31).—Japanese acid clay is an effective dehydration catalyst for the prep. at 350—400° of MeCN and PhCN; yield 85%. CH. ABS.

Decomposition of lead tetraethyl in ethylene and hydrogen in benzene. P. L. CRAMER (J. Amer. Chem. Soc., 1934, 56, 1234—1238).—Thermal decomp. of PbEt_4 in C_6H_6 in absence and presence of varying amounts of H_2 and C_2H_4 at 180—275° is studied. Reaction occurs in the liquid phase, the C_6H_6 acts as solvent only, H_2 takes little or no part, and C_2H_6 and a little C_4H_{10} are the paraffin hydrocarbons produced; CH_4 is not formed. Evidence is given favouring the assumption that the main reaction of Et radicals in solution is $2\text{Et} \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$; the C_2H_4 is then converted into higher hydrocarbons (reaction being induced by Et). Large amounts of C_2H_4 are converted into light-coloured oils by the simultaneous decomp. of PbEt_4 ; these reactions are probably induced by Et. H. B.

Indium trimethyl. L. M. DENNIS, R. W. WORK, and E. G. ROCHOW [with E. M. CHAMOT] (J. Amer. Chem. Soc., 1934, 56, 1047—1049).—The prep. and properties of *InMe}_3*, m.p. 89—89.5°, are described. The mol. wt. in freezing C_6H_6 indicates $(\text{InMe}_3)_4$. E. S. H.

Constitution of β -carotene. R. KUHN and H. BROCKMANN (Ber., 1934, 67, [B], 885—888).—A complete scheme is given of the course of the fractional oxidation of β -carotene (I) and azafrin (II) with CrO_3 . (I) is thereby proved to be α -di-2 : 2 : 6-trimethyl- Δ^6 -cyclohexenyl- $\gamma\eta\mu\pi$ -tetramethyloctadecanonaene, the crucial point being the identity of the dehydroazafrinonamides,



derived from (I) or (II).

H. W.

Further instances of formation of chlorobenzene from magnesium phenyl bromide and chlorinated substances. R. J. W. LE FÈVRE and P. J. MARKHAM (J.C.S., 1934, 703—705; cf. A.,

1932, 862).—PhCl is formed in 60% yield from MgPhBr (I) and EtOCl in Et₂O: MgPhBr+EtOCl → PhCl+OEt·MgBr. (I) and PhSO₂Cl give Ph₂SO₂ (in agreement with Hepworth and Clapham, J.C.S., 1921, 119, 1188; cf. Wedekind and Schenk, A., 1921, i, 664), a little PhSO₂H, and about 25% of PhCl (MgPhBr+PhSO₂Cl → PhCl+PhSO₂·MgBr). *p*-C₆H₄Me·SO₂Cl (II) and (I) afford slightly <25% of PhCl. (II) and MgEtBr give EtCl. PhCl is not produced from (I) and PhICl₂; some chlorination of the Et₂O occurs. H. B.

Halogenation. VIII. Bromination and iodination of monochlorotoluenes. P. S. VARMA and V. SAHAY (J. Indian Chem. Soc., 1934, 11, 293—294; cf. A., 1916, i, 469).—*o*- or *m*-C₆H₄MeCl with Br in AcOH containing HNO₃ or H₂SO₄ at 100° during 2—4 hr. affords 2-chloro-5-bromo- and a mixture (3:1) of 3-chloro-4-bromo- and 3-chloro-6-bromo-toluene. *p*-C₆H₄MeCl affords similarly *p*-C₆H₄Cl·CH₂Br. *o*-C₆H₄MeCl and I in AcOH containing NaNO₂ and oleum at 100° during 4 hr. afford 2-chloro-5-iodotoluene. *m*-C₆H₄MeCl affords similarly 3-chloro-6-iodotoluene. J. L. D.

Influence of poles and polar linkings on tautomerism in the simple three-carbon system.

III. Benzyl Δ^α- and Δ^β-propenyl sulphones. E. ROTHSTEIN (J.C.S., 1934, 684—687).—CH₂Ph·SO₂Na (prep. of acid described) and allyl bromide in EtOH give benzyl Δ^β-propenyl sulphone (I), m.p. 64—65°, oxidised (O₃) to benzylsulphonylacetaldehyde (*p*-nitrophenylhydrazone, m.p. 195—196°); prolonged treatment with O₃ affords benzylsulphonylformaldehyde (*p*-nitrophenylhydrazone, m.p. 178—180°). Benzyl β-hydroxypropyl sulphone (II), m.p. 98—99°, prepared by oxidation (H₂O₂, AcOH) of the sulphide, b.p. 55—56°/11 mm. (from CH₂Ph·SNa and CH₂Cl·CHMe·OH), and PCl₅ in CHCl₃ give benzyl β-chloropropyl sulphone (III), m.p. 88°, converted by boiling C₅H₅N into benzyl Δ^α-propenyl sulphone (IV), m.p. 83·6° (ozonolysis product, BzOH). α,β-Dibenzylthiolpropane, b.p. 218—222°/14 mm. (from CH₂Ph·SNa and CH₂Br·CHMeBr in 80% EtOH), is oxidised (H₂O₂, AcOH) to the disulphone, m.p. 201°. Direct interconversion of (I) and (IV) could not be effected; treatment with NaOR (R=H or Alk) gives CH₂Ph·SO₂·CH₂·CHMe·OR in each case. (I) and (IV) with HI (*d* 1·9) afford benzyl β-iodopropyl sulphone, m.p. 105—107°, hydrolysed (aq. EtOH-NaOH) to (II). Benzyl β-methoxypropyl sulphone (V), b.p. 214°/14 mm. [from (III) and MeOH-KOH], is demethylated (HI-AcOH) to (II). (I), (II), (IV), and (V) are decomposed by boiling 3*N*-KOH to CH₂Ph·SO₂Me and MeCHO. Benzyl γ-hydroxypropyl sulphone (VI), m.p. 127°, prepared by oxidation (H₂O₂, AcOH) of the sulphide, b.p. 185°/19 mm. (from CH₂Ph·SNa and CH₂Cl·CH₂·CH₂·OH in EtOH), is stable to 3*N*-KOH; with KHSO₄ at 220°, di-(γ-benzylsulphonylpropyl) ether, m.p. 111—112°, is formed. Benzyl γ-chloropropyl sulphone, m.p. 96° [from (VI) and PCl₅ in CHCl₃], is converted by C₅H₅N or EtOH-KOH into (VI). Me Δ^β-propenyl sulphone, b.p. 130°/15 mm., from (MeSO₂)₂Mg and allyl bromide in Et₂O, is decomposed by 3*N*-KOH to MeCHO. H. B.

Reduction of phenylated olefines with alkali metals in liquid ammonia. C. B. WOOSTER and J. F. RYAN (J. Amer. Chem. Soc., 1934, 56, 1133—1136).—CHPh:CH₂ (I) and excess of Na in liquid NH₃ give PhEt and polymerised (I); CHPh:CHPh affords CH₂Ph·CH₂Ph (formed by ammonolysis of the intermediate CHNaPh·CHNaPh); CPh₂:CH₂ yields (mainly) CNaPh₂Me and CNaPh₂·CH₂·CH₂·CNaPh₂ [ammonolysis of the ·CNaPh₂ group does not occur (cf. A., 1932, 838)], which are converted by NH₄Cl into CHPh₂Me and CHPh₂·CH₂·CH₂·CHPh₂, respectively; CPh₂:CHPh furnishes CNaPh₂·CH₂Ph (cf. *loc. cit.*); CPh₂:CPh₂ (II) gives CNaPh₂·CNaPh₂ (III) and some CHNaPh₂ (or CNaPh₂?), since treatment with EtBr affords CHPh₂·CHPh₂ (IV) and CHPh₂Et whilst decomp. with NH₄Cl yields (IV) and CH₂Ph₂; CPh₂:CHMe furnishes CNaPh₂Et (cf. *loc. cit.*); CPh₂:CH·CHPh₂ gives CNaPh₂·CH₂·CHPh₂, hydrolysed (NH₄Cl) to CHPh₂·CH₂·CHPh₂ (V) and converted by Me₂SO₄, EtBr, and CH₂PhCl into αγγγ-tetraphenylbutane (VI), m.p. 118° [also prepared by reduction (Na, EtOH) of αγγγ-tetraphenyl-Δ^α-butene], αγγγ-tetraphenylpentane (VII), m.p. 128°, and (probably) αγγδ-pentaphenylbutane (VIII), m.p. 122—123°, respectively; CPh₂:C:CPh₂ (IX) affords CNaPh₂·CH₂·CNaPh₂, hydrolysed (NH₄Cl) to (V). (III), obtained from (II) and 2 equivs. of Na in liquid NH₃, when treated with dry air, Me₂SO₄, or CH₂PhCl regenerates (II). Hydrolysis (H₂O) of the product from (IX) and 2 equivs. of Na gives CPh₂:CH·CHPh₂, indicating that addition of Na to (IX) occurs in stages. Treatment of the product from (IX) and excess of K with Me₂SO₄, EtBr, and CH₂PhCl affords (VI), (VII), and (VIII), respectively; a small amount of a second product (not identified) was formed in each case. H. B.

Conjugated systems. XV. Addition of hydrogen chloride to the geometrical isomerides of phenylbutadiene. I. E. MUSKAT and K. A. HUGGINS (J. Amer. Chem. Soc., 1934, 56, 1239—1241).—*trans*-α-Phenylbutadiene and HCl in cold Et₂O give *trans*-γ-chloro-α-phenyl-Δ^α-butene, b.p. 103°/5 mm. (A., 1931, 349) (ozonolysis product, PhCHO). *cis*-α-Phenylbutadiene (I) similarly affords the unstable *cis*-γ-chloro-α-phenyl-Δ^α-butene, b.p. 106°/5 mm. (ozonolysis products, PhCHO and CHClMe·CHO), converted by 10% NaOH at room temp. into (I), and by Ag₂O in H₂O into *cis*-styrylmethylcarbinol (*loc. cit.*). The above results are in accordance with the theory previously developed (A., 1930, 451). H. B.

Iodination in liquid ammonia. T. H. VAUGHN and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1934, 56, 1207—1209).—α-Iodo-β-2:4:6-trimethylphenyl-, m.p. 91·8—92·2°, -β-xylyl-, b.p. 121—122° (slight decomp.)/4 mm., -β-*o*-, m.p. 37·7—38°, -*m*-, m.p. 11·1°, and -*p*-, m.p. 84·7—85°, -chlorophenyl-, -β-*p*-bromophenyl-, m.p. 93·8—94°, and -β-α'-methylvinyl- (I), b.p. 80·8—81°/72 mm., -acetylenes are prepared from the appropriate CH:CR and I in liquid NH₃; they are unstable to light and heat. (I) polymerises in presence of O₂ to a black solid. α-Chloro-2:4:6-trimethylstyrene, b.p. 122—124°/25 mm. (from 2:4:6-C₆H₂Me₃·COMe and PCl₅), and NaNH₂ in mineral

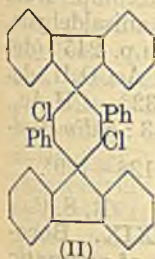
oil at 150° give 2:4:6-trimethylphenylacetylene, b.p. 100.6—101.5°/20 mm. (lit. 168—175°/20 mm.), m.p. 2.7—3.5° (*Hg* derivative, m.p. 238.5—239°). *α*-*Dichlorostyrene*, b.p. 115—116°/20 mm. (from *p*-C₆H₄Cl·COMe and PCl₅), and 25% EtOH-KOH afford *p*-chlorophenylacetylene, m.p. 45.5—46.1° (*Hg* derivative, m.p. 221.5—222°). Of the CH:CR so far examined, those where R is unsaturated and conjugated with C:C are readily and completely iodinated.

H. B.

Condensation reactions under pressure. II. Formation of diphenyl from benzene by heat under pressure in the presence of catalysts. J. P. WIBAUT, H. M. ROMIJN, and H. D. T. WILLINK (Rec. trav. chim., 1934, 53, 584—590; cf. A., 1931, 632).—The yield of Ph₂ from C₆H₆ is increased by pressure, being about 4—5% at 440—450°/170 atm. This is increased to 7.4% by a Ni catalyst, to 14—17% by 6% of I at 420—440°/125 atm., and to 9% by 10% of HI at 420°/120 atm.

R. S. C.

Attempted preparation of rubene derivatives from fluorene with production of a red compound not derived from rubene. Ring tension and probability of rubene formation. C. DU-FRAISSE and A. P. DE CARVALHO (Compt. rend., 1934, 198, 1615—1617).—*Phenylethinenylylfuorenol*, m.p. 83—83° (from CH:CPH and fluorenone), is readily isomerised to fluorenylideneacetophenone, but attempts to remove HCl from the corresponding chloride (I) give a red non-fluorescent substance, C₁₂H₂₆Cl₂, possibly (II), m.p. 290° (block), which has not the absorption spectrum of a rubene derivative



and with O₂ in light gives only very slowly a non-dissociable product. An intermediate product from (I) is a colourless substance, m.p. 120—121° (block) (containing 10.63% of Cl), which, when heated, gives (II), and a yellow Cl-free substance, m.p. 250° (block). Attachment of rings to the C₆ rings forming part of the rubene skeleton introduces such strain that the compound cannot be prepared.

R. S. C.

Synthesis of thiocarbamide derivatives. I. K. MURATA (J. pr. Chem., 1934, [ii], 140, 8).—CH₂Cl·CO₂Et reacts with cold CS(NHPh)₂ and MgMeI in Et₂O to give the *Et* ester, m.p. 176°, *thiocarbamilodiacetic acid*, CS(NPh·CH₂·CO₂H)₂, m.p. 144° (*Me* ester, m.p. 148°).

J. W. B.

Third hydrate of phenylmethylethylbetaine, and its conditions of formation. (MME.) GUAISNET-PILAUD (Compt. rend., 1934, 198, 1520—1522).—MeI and NPhEt·CH₂·CO₂Et (I) (prepared from CH₂Cl·CO₂Et and NPhEt at 150°) afford a product which with Ag₂O gives a mixture of phenylmethylethylbetaine dihydrate, m.p. 79.5°, and a *monohydrate* (II), m.p. 103° (*picrate*, m.p. 186°; *chloroplatinate*, m.p. 168°), isomeric with the monohydrate of m.p. 175° (cf. A., 1933, 948). If (I) is prepared from CH₂I·CO₂Et and NPhMeEt followed by decomp. with Ag₂O, (II) only is obtained.

J. L. D.

Reactions of aromatic amine-oxides and of phenylhydroxylamine. E. HOPE (Chem. and Ind.,

1934, 425).—Formation of *o*- and *p*-NMe₂·C₆H₄·SO₃H and -NMe₂·C₆H₄·NO₂ from NPhMe₂ oxide and SO₂ and NO₂ and of *p*-OH·C₆H₄·NH₂, *p*-OEt·C₆H₄·NH₂, and *p*-C₆H₄Cl·NH₂ from NPh·OH is explained by anionoid addition to the cations ⁺NPhMe₂·OH and ⁺NH₂Ph·OH, respectively.

S. C.

Derivatives of salicylic acid. V. Synthesis and constitution of 2-nitrotoluene-6-sulphonic acid. A step towards the synthesis of 6-sulphosalicylic acid. N. W. HIRWE and M. R. JAMBHEKAR (J. Indian Chem. Soc., 1934, 11, 239—242; cf. A., 1933, 607).—4-Nitrotoluene-2-sulphonic acid in H₂SO₄ and HNO₃ (*d* 1.51) at 100° during 3 hr. affords 2:4-dinitrotoluene-6-sulphonic acid (I), m.p. 120° [Pb, K(+2H₂O), Na, Ca (+4H₂O), and Ba (+4H₂O) salts], which with PCl₅ affords the *sulphonyl chloride*, m.p. 107°, which does not give the *sulphonamide* with NH₃. (I) with boiling EtOH-(NH₄)₂S during 2 hr. affords 2-nitro-*p*-toluidine-6-sulphonic acid (II), m.p. 270° (decomp.) [K salt, which with PCl₅ gives the *sulphonyl chloride*, m.p. > 260° (decomp.), converted by NH₃ into the *sulphonamide*, m.p. 230°], also obtained from 2-nitro-*p*-toluidine with oleum at 100° during 6 hr. The diazonium derivative of (II) with boiling EtOH during 3 hr. affords 2-nitrotoluene-6-sulphonic acid [+2H₂O, m.p. 127°; Ba salt (+8H₂O); *sulphonamide*, m.p. 165°]. 2:4-Dinitrotoluene cannot be sulphonated.

J. L. D.

New case of molecular asymmetry. A. SEMENTZOV (Ukrain. Chem. J., 1933, 8, 193—195).—*o*-Toluidine-3:5-disulphonic acid (I) yields insol. salts with strychnine and brucine; the acid regenerated from the former, but not the latter, salt has α +0.35°, pointing to the partial resolution of (I). This result supports the octahedral or prismatic structure of the C₆H₆ mol.

R. T.

Hexahydrodiphenylamine and its derivatives. H. T. BUCHERER and H. FISCHBECK (J. pr. Chem., 1934, [ii], 140, 69—89).—Condensation of cyclohexyl bromide (I) with the appropriate NH₂Ar and subsequent treatment with NaCl or alkali followed by HCl affords the *hydrochlorides* of cyclohexyl-aniline, -*p*-, m.p. 205°, and -*o*-toluidine, m.p. 126°, - α -, m.p. 187°, and - β -naphthylamine, m.p. 261°, and -*p*-phenylenediamine, m.p. 267° [4-*Ac* derivative, m.p. 311°, of the free base from (I) and NH₂·C₆H₄·NHAc]. Condensation is not effected in the presence of NaOH alone, but with NaOH-Cu powder the hydrobromide is obtained. Primary bases (NH₂Ph) may be separated from *sec.* (NHPHMe; 99% recovery) by their interaction with OH·CH₂·SO₃Na at 80—100°. In C₆H₆ solution cyclohexanone (II), KCN, and NH₂Ph·HCl (or NH₂Ph with passage of dry HCl) afford the nitrile (III), m.p. 73°, of 1-anilinocyclohexane-1-carboxylic acid, m.p. 158° (*amide*, m.p. 148°), *o*-NH₂·C₆H₄·CO₂H similarly giving *o*-1-cyanocyclohexylaminobenzoic acid (IV), m.p. 168° (1-carboxylamido-compound, m.p. 218°). Alternatively the cyanohydrin (V) of (II) (from the NaHSO₃ compound and KCN) is condensed with NH₂Ph (but not with NHPHMe; hence separation of primary and *sec.* bases) to give (III), and with the appropriate arylamine to give the *nitrile* of 1-*o*-, m.p. 76° (*amide*, m.p.

224°), and 1-*p*-toluidino-, m.p. 79°, 1-*p*-aminoanilino-, m.p. 200° (p-*N*-Ac derivative, m.p. 143°; amide, m.p. 263°), 1-*m*-aminotoluidino-, m.p. 130°, 1- α -, m.p. 135° (amide, m.p. 143°), and 1- β -naphthylamino-, m.p. 122°, -cyclohexane-1-carboxylic acid, and (IV). With 2 mols. of the appropriate diamine at 34–40° are obtained NN'-dicyclohexyl-*p*-phenylenediamine-1:1'-dicarboxylamide, m.p. 280°, through the nitrile, m.p. 169°, and corresponding derivatives from *m*-phenylenediamine, m.p. 207° and 116°. With (NH₄)₂CO₃ (V) gives a substance, m.p. 215°, hydrolysed by 50% H₂SO₄ to give the sulphate of the NH₂-acid.

J. W. B.

Nuclear alkylation of aromatic bases. II. Action of methyl alcohol on the hydrochlorides of 2- and 4-aminodiphenyl. D. H. HEY and E. R. B. JACKSON (J.C.S., 1934, 645–649; cf. A., 1931, 950).—4-Aminodiphenyl hydrochloride (1 mol.) and MeOH (1.5 mols.) at 250–300° for 12 hr. (all experiments are carried out in an electrically-heated Monel metal autoclave) give unchanged material and some didiphenylamine, m.p. 205°; carbonisation also occurs. With 3 mols. of MeOH, 4-amino-3:5-dimethyl- and 4-amino-3:5:4'-trimethyl- (I) -diphenyls are formed; 4-amino-3-methyldiphenyl (which must be an intermediate) could not be detected. A small amount of (I) is obtained using 6 mols. of MeOH; the major portion of the product consists of *sec.*- and *tert.*-bases. 2-Aminodiphenyl hydrochloride and 3 mols. of MeOH similarly give mainly *tert.* (A), some *sec.*-, and practically no primary base. (A) and MeI afford the *methiodide*, m.p. 293–295° (decomp.), of a dimethylphenanthridine [*picrate*, m.p. 241° (decomp.)]. In all the above experiments some separation of N from the nucleus occurs, since volatile bases are liberated when the reaction product is treated with alkali; evidence of phenol formation (cf. *loc. cit.*) was not obtained.

*cyclo*Hexanone and Mg *m*-5-xylyl bromide (II) give 1-*m*-5-xylylcyclohexanol, b.p. 150–160°/20 mm., dehydrated (HCO₂H; Sherwood *et al.*, A., 1932, 843) to 1-*m*-5-xylyl- Δ^1 -cyclohexene, b.p. 157–158°/20 mm., which is dehydrogenated (S in quinoline at 250°) to 3:5-dimethyldiphenyl, b.p. 273–276°. Successive treatment of this with HNO₃ (*d* 1.42) in AcOH, SnCl₂-conc. HCl, and Ac₂O gives 4-acetamido-3:5-dimethyldiphenyl, m.p. 200–201°, oxidised (CrO₃, AcOH) to BzOH. 4-Methylcyclohexanone (III) and (II) afford 1-*m*-5-xylyl-4-methylcyclohexanol, b.p. 154–164°/20 mm.; the cyclohexene is dehydrogenated (S) to 3:5:4'-trimethyldiphenyl, m.p. 44–45° (4-NO₂-derivative, m.p. 94–95°); 4-Acetamido-3:5:4'-trimethyldiphenyl, m.p. 241–242°, is oxidised by CrO₃-AcOH to *p*-C₆H₄(CO₂H)₂ and by neutral KMnO₄ to 4-acetamidodiphenyl-3:5:4'-tricarboxylic acid (*Et* ester, m.p. 129–130°). 3:4'-Dimethyldiphenyl is similarly prepared from 1-*m*-tolyl-4-methylcyclohexanol, b.p. 155–165°/20 mm. [from (III) and *m*-C₆H₄Me-MgBr]. 2-Aminodiphenyl is methylated (Me₂SO₄ at 150°) to 2-dimethylaminodiphenyl (IV) [*methiodide*, m.p. 228° (decomp.)]; with MeI and aq. Na₂CO₃ (IV) and some 2-methylaminodiphenyl are produced. The *methiodide*, m.p. 260° (decomp.) (lit. 247°), of 9-methylphenanthridine (Morgan and Walls, A., 1931, 1308) [*picrate*, m.p. 248° (decomp.)

(lit. 233°)] is prepared for comparison with that from (A). H. B.

Relative reaction velocities of amines with phenylcarbimide.—See this vol., 604.

Dimethyldihydroresorcinol. III. Azo-dyes and diazo-oxy-compounds. B. H. IYER and G. C. CHAKRAVARTI (J. Indian Inst. Sci., 1934, 17, A, 41–47).—Dimethyldihydroresorcinol with PbN₂Cl in the presence of acid gives benzeneazodimethyldihydroresorcinol, m.p. 142° (diphenylhydrazone, m.p. 191–192°). The following are similarly obtained: *o*-, m.p. 125°, *m*-, m.p. 122–123°, and *p*-toluene-, m.p. 156–157° (diphenylhydrazone, m.p. 185°), α -, m.p. 141°, and β -naphthalene-, m.p. 200°, and *p*-sulphobenzene-azodimethyldihydroresorcinol, decomp. 360° (shrinks 300°). In an alkaline medium alkali-insol. substances are obtained, which are considered to be diazo-oxy-derivatives. Those from diazotised NH₂Ph and *o*-, *m*-, and *p*-C₆H₄Me-NH₂ have the same m.p. as the true azo-compounds, into which they are converted by heat and by alkali. Those from α - and β -C₁₀H₇-NH₂ are less readily converted, and have m.p. 200° (decomp.) and 255° (decomp.), respectively.

A. A. L.

Derivatives of *p*-dihydrazinobenzene. H. A. J. SCHOUTISSEN (Rec. trav. chim., 1934, [iv], 53, 561–566).—*p*-C₆H₄(NH-NH₂)₂·2HCl and NaNO₂ in conc. HCl at 0° give *p*-bistriazobenzene (*p*-phenylenediazide), m.p. 83°, and with NaOAc in aq. EtOH it forms dihydrazones with the following CO-compounds: PhCHO, m.p. 251° (decomp. from 225°), *o*-OH-C₆H₄·CHO, m.p. about 255° (decomp. from 200°), vanillin, m.p. 230° (decomp.), anisaldehyde, m.p. 225–230° (decomp.), piperonal, m.p. 245° (decomp.), C₆H₅CO, m.p. 214° (decomp.), AcCO₂H, decomp. 174°, and CH₂Ac·CO₂Et, m.p. 132°. CH₂Ac₂, however, gives *p*-phenylene-1:1'-bis-3:5-dimethylpyrazole, *p*-C₆H₄(N<NMe·CMe<CO-CH)₂, m.p. 128–129°.

R. S. C.

Aromatic fluorine compounds. XIX. Borofluoride process for the preparation of aromatic fluorine compounds. G. SCHEMANN and (in part) R. PILLARSKY, W. WINKELMÜLLER, T. B. MAU, and H. G. BAUMGARTEN (J. pr. Chem., 1934, [ii], 140, 97–116).—A full bibliography and discussion of the technique of the prep. of aromatic F-derivatives by the decomp. of the diazonium borofluoride. The (improved) prep. of the following is described (% yields in parentheses): *o*- (44) and *m*-C₆H₄F₂ (68), 1:2:4-C₆H₃F₃ from 2:4- (17) or 2:5- (55) (*Bz* derivative, m.p. 115°) -C₆H₃F₂-NH₂, PhCl (65) from the stannichloride, decomp. 110°, of PhN₂Cl, *o*-C₆H₄F·OH (82) from its Me ether, and *o*-C₆H₄F·CO₂H (45) from *o*-carbethoxybenzenediazonium borofluoride, decomp. 105–106°. Free OH and CO groups are unfavourable to the reaction and should be protected.

J. W. B.

Coupling of α -amino-acids with diazonium salts. M. BUSCH, N. PATRASCANU, and W. WEBER (J. pr. Chem., 1934, [ii], 140, 117–128).—NH₂·CH₂·CO₂H (I) couples with PhN₂Cl (II) in *N*-NaOH at 0° to give (45–48% yield) di(benzene-diazo)aminoacetic acid (III), decomp. 124°, decomp.

posing in HCl-EtOH to give $\text{PhN}_2\cdot\text{NPh}$ (IV), MeCl , CO_2 , and N_2 . With NH_2Me (II) gives $(\text{PhN}_2)_2\text{NMe}$, similarly decomposed to (IV). The product from (I) and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ (V) decomposes more readily, to a mixture of *di*-(*p*-nitrobenzene-diazo)aminoacetic acid, decomp. $166\text{--}167^\circ$ (26%), and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ (VI) (20%). In absence of NaOH the clear solution obtained slowly decomposes with increasing formation of (VI). The Et ester of (I) with (II) affords (III) (due to hydrolysis) and a substance, $\text{C}_8\text{H}_7\text{ON}_3$, m.p. 134° (decomp.), probably $\text{CO} \begin{array}{l} \text{CO} \\ \text{CH}_2 \end{array} \text{N}\cdot\text{N}_2\text{Ph}$ or $\text{CO} \begin{array}{l} \text{NPh}\cdot\text{N} \\ \text{CH}_2\text{--N} \end{array}$, but with (V) in presence of NaOAc is obtained *Et p*-nitrobenzene-diazoaminoacetate, m.p. 99° (63% yield), hydrolysed by aq. NH_3 to the corresponding acid, m.p. 163° . With (V) alanine gives (VI) and an unidentified substance, m.p. 117° ; sarcosine affords its *p*-nitrobenzene-diazo-derivative, m.p. $107\text{--}108^\circ$ (45% yield), and tyrosine gives 3:5-*di*-*p*-nitrobenzeneazotyrosine (ring coupling), m.p. 175° . J. W. B.

Reactivity of resorcinol monoalkyl ethers towards diazonium compounds. H. H. HODGSON, R. J. H. DYSON, and (in part) H. CLAY (J.C.S., 1934, 629—631).—4-Benzeneazoresorcinol 3-Me (I), m.p. $137\text{--}138^\circ$, 3-Et (II), m.p. 145° , 3-Pr^a (III), m.p. 117° , and 3-Pr^b (IV), m.p. 92° , ethers are prepared by slow addition of a cold solution of PhN_2Cl (1 mol.) [freed from HNO_2 by $\text{CO}(\text{NH}_2)_2$ and HCl by NaOAc] to a well-stirred solution of $m\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{OR}$ (1 mol.) in EtOH+aq. NaOAc. Witli 2 mols. of PhN_2Cl , 4:6-bisbenzeneazoresorcinol 3-Me ether (V), m.p. 190° [not the 2:4-derivative as stated by Orndorff and Thebaud (A., 1901, i, 774)] [also prepared from (I)], and 3-Et ether (VI), m.p. 147° , are obtained; disubstituted derivatives do not accompany (III) and (IV), and coupling does not occur with $m\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{OBu}^a$. Repression of ionisation by Oalk progressively deactivates C_4 as the series is ascended. (V) and (VI) with HNO_3 (*d* 1.42) at $30\text{--}40^\circ$ give the 2- NO_2 -derivatives, m.p. 228° and 225° , respectively. 6-Nitro-2:4-bisbenzeneazoresorcinol 3-Me, m.p. 142° , and 3-Et, m.p. 126° , ethers are prepared from 6-nitroresorcinol 3-alkyl ether (1 mol.) and PhN_2Cl (2 mols.). (I)–(IV) are de-alkylated to 4-benzeneazoresorcinol. (I) and (II) are reduced to 4-aminoresorcinol 3-Me and 3-Et ether, respectively, whilst (III) and (IV) are readily methylated (CH_3N_2 ; Me_2SO_4 -alkali) thus indicating coupling in the *p*-position to the OH (cf. Orndorff and Thebaud, *loc. cit.*). A mixture of (I) and (V) is always produced if alkali hydroxide is present in the coupling medium. 4-o-Nitrobenzeneazoresorcinol 3-Me, m.p. 189° , 3-Et, m.p. 167° , 3-Pr^a, m.p. 133° , 3-Pr^b, m.p. 115° , and 3-Bu^a, m.p. 88° ; 4-m-nitrobenzeneazoresorcinol 3-Me, m.p. 153° , 3-Et, m.p. 125° , 3-Pr^a, m.p. 114° , 3-Pr^b, m.p. 95° , and 3-Bu^a, m.p. 86° , and 4-*p*-nitrobenzeneazoresorcinol 3-Me, m.p. $198\text{--}199^\circ$, 3-Et, m.p. $185\text{--}187^\circ$, 3-Pr^a, m.p. $156\text{--}157^\circ$, 3-Pr^b, m.p. $145\text{--}146^\circ$, and 3-Bu^a, m.p. $149\text{--}150^\circ$, ethers are described; the decrease in m.p. as the series is ascended is attributed to a form of co-ordination which increases in intensity with the size of the alkyl group. 4-*p*-Chlorobenzeneazoresorcinol 3-Me, m.p. 142° , and 3-Et, m.p. 133° , and 4-*p*-sulpho-

benzeneazoresorcinol 3-Pr^a, decomp. when heated, and 3-Pr^b ethers are also described. H. B.

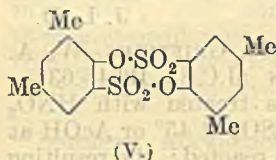
Additive compound of phenol and hexamethylenetetramine. L. H. SMITH and K. N. WELCH (J.C.S., 1934, 729—730).—Interaction of CH_2O , NH_3 , and PhOH affords $\text{C}_6\text{H}_{12}\text{N}_4\cdot 3\text{C}_6\text{H}_6\text{O}$ (I) (cf. A., 1893, i, 298) together with a compound, $\text{C}_6\text{H}_{12}\text{N}_4\cdot\text{C}_6\text{H}_6\text{O}$, m.p. $176\text{--}176.5^\circ$ (decomp.), which with excess of PhOH gives (I). J. L. D.

Nitration of anisole. P. H. GRIFFITHS, W. A. WALKER, and H. B. WATSON (J.C.S., 1934, 631—633).—PhOMe (I) (1 mol.) is treated with HNO_3 (*d* 1.42) (1 mol.) alone or in H_2SO_4 at 45° or AcOH at 65° until about 70% of (I) has reacted; the resulting mixture (yield 30%) of $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ contains *o*- (30.8—45%), *m*- (1.3—1.7%), and *p*- (53.5—67.5%). With HNO_3 (*d* 1.42 and 1.5) in Ac_2O at 10° , the mixture (99% yield) contains *o*- (69.4—71.5%), *m*- (2.2—2.3%), and *p*- (26.3—28.4%); benzoyl nitrate (from BzCl and AgNO_3) in CCl_4 at 0° gives *o*- (63.5%), *m*- (1.9%), and *p*- (34.6%). Contrary to Francis (A., 1907, i, 53), the use of acyl nitrate does not lead to exclusive *o*-nitration. The results provide some confirmation of Arnall's work (A., 1924, i, 636) on the nitration of PhOH. The composition of the above mixtures [shown to be free from (I) or $(\text{NO}_2)_2$ -derivative] is determined by thermal analysis. H. B.

Condensation of *o*-anisidine with formaldehyde and benzaldehyde. E. BUREŠ and Z. SCHLESINGER (Časopis českoslov. Lék., 1933, 13, 165—175; Chem. Zentr., 1933, ii, 2663).—Condensation of *o*-anisidine (I) with CH_2O yields *N*-methylene-*o*-anisidine (II), m.p. 85° , and *NN'*-methylenedi-*o*-anisidine, m.p. 155° . (II) with NaHSO_3 gives *Na o*-anisylaminomethanesulphonate, decomp. 200° ; with HgCl_2 , the compound $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CH}_2\cdot\text{HgCl}_2$, decomp. $150\text{--}160^\circ$; and a picrate, decomp. 160° . The NO-compound of (II) with $\beta\text{-C}_{10}\text{H}_7\cdot\text{ONa}$ forms 5-*di*(hydroxynaphthyl)amino-*N*-methylene-*o*-anisidine. The corresponding *N*-benzylidene derivative forms red crystals. (I) with PhCHO yields benzylidene-*o*-anisidine, m.p. $56\text{--}57^\circ$ (NaHSO_3 compound, decomp. 200° ; HgCl_2 compound, decomp. 120° ; picrate, decomp. $140\text{--}150^\circ$). These condensation products are very labile. H. J. E.

***m*-Xylenols.** G. LER (Anilinokras. Prom., 1934, 4, 77—84).—*m*-5-Xylenol (I) and SO_2Cl_2 afford 5-hydroxy-*m*-xylene-2:4-disulphonyl chloride (II), m.p. $117\text{--}119^\circ$, and an isomeride (III), m.p. $89\text{--}91^\circ$; these yield the corresponding sulphonanilides, m.p. $205\text{--}207^\circ$ and $160\text{--}161^\circ$, respectively. With NH_3 in Et_2O (II) affords the disulphonamide, m.p. $206\text{--}208^\circ$, whilst (III) yields unstable products. (II) when heated with NaOAc in COMe_2 affords 1:3-dimethyl-2:5-sulphobenzquinone-4-sulphonyl chloride, m.p. $>300^\circ$; under similar conditions (III) yields only oily products. The conc. HCl solution of the product of reaction of (I) and ClSO_3H acid yields with H_2O_2 at 0° the 2:4:6- Cl_3 -derivative of (I), m.p. $175\text{--}177^\circ$, which is also obtained, together with *K* 2:6-dichloro-5-hydroxy-*m*-xylene-4-sulphonate, m.p. $>300^\circ$, by adding H_2O_2 to the acidified products of alkaline hydrolysis of (II). Reduction of (II) with Zn and AcOH yields 5-hydroxy-2:4-dithiol-*m*-xylene,

m.p. 75° (*Bz*₃, m.p. 160—161°, and *Ac*₃ derivative, m.p. 124—125°; *dipicrate*, m.p. 237—238°), which when heated at 100° during 3—4 hr. with aq. $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$ and KOH affords the corresponding 2:4-dithioglycollic acid derivative, m.p. 151°. 4-Hydroxy-*m*-xylene-5-sulphonyl chloride (IV) [5-sulphonanilide, m.p. 142—143° (*N-Me*, m.p. 111—112°, and 4-*Ac* derivative, m.p. 105°); 4-*Ac* derivative, m.p. 62°] affords the



sulphonyl chloride (V), m.p. > 300°, when heated with 2*N*-KOH, with NaOAc in COMe_2 , or on passing NH_3 into its Et_2O solution. With Zn and AcOH (IV) affords 4-hydroxy-5-thiol-*m*-xylene (VI), m.p. 91—93° (*Bz*₂ derivative, m.p. 72°; *monopicrate*, m.p. 164°), which when heated with KOH and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ yields *m*-xylene-4-glycollic-5-thioglycollic acid, m.p. 155°. *m*-4-Xylenol and diazotised *m*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ (VII) afford 5-*m*-nitrobenzeneazo-4-hydroxy-*m*-xylene, m.p. 194—195°; (IV) and (VI) do not react with (VII).

Oxidation of *p*-*n*-propylphenol to 2-*n*-propylquinol. G. BADDELEY and J. KENNER (J.C.S., 1934, 633—634).—*m*- $\text{C}_6\text{H}_4\text{Pr}^a\cdot\text{OH}$ and dil. HNO_3 in C_6H_6 give (after removal of *o*-nitrophenols in steam) 4-nitro-3-*n*-propylphenol (I), b.p. 157°/0.6 mm., m.p. 58°; using Schultz's conditions (A., 1907, i, 1030), a dinitro-*m*-propylphenol, b.p. 145°/0.5 mm., m.p. 125°, results. (I) is reduced (Sn, HCl) to the NH_2 -compound (*Ac* derivative, m.p. 140°), oxidised (aq. FeCl_3) to *n*-propyl-*p*-benzoquinone, which is reduced (H_2SO_3) to *n*-propylquinol (II), m.p. 90°. (II) is also formed when *p*- $\text{C}_6\text{H}_4\text{Pr}^a\cdot\text{OH}$ is oxidised with Caro's acid at 70—80°; this reaction is an expanded form of the conversion of glycolaldehydes into α -hydroxyketones (Danilov and Danilova, A., 1928, 64; 1929, 1448; 1931, 90; 1933, 1277): $\text{OH}\cdot\text{CR}_2\cdot\text{CHO} + \text{H}^+ \rightarrow \text{OH}\cdot\text{CR}_2\cdot\text{CH}^+\cdot\text{OH} \rightarrow \text{COR}\cdot\text{CHR}\cdot\text{OH} + \text{H}^+$. The analogous isomerisation of $\text{CR}_3\cdot\text{CHO}$ is: $\text{CR}_3\cdot\text{CHO} + \text{H}^+ \rightarrow \text{CR}_3\cdot\text{CH}^+\cdot\text{OH} \rightarrow \text{CR}_2\cdot\text{CHR}\cdot\text{OH} \rightarrow \text{CHR}_2\cdot\text{COR} + \text{H}^+$.

H. B.

Synthesis of halogenated thiophenols. R. C. DOSSER and G. H. RICHTER (J. Amer. Chem. Soc., 1934, 56, 1132—1133).—2-Chlorotoluene-5-sulphonyl chloride, m.p. 64°, is reduced (Zn and HCl in C_6H_6) to 6-chloro-*m*-thiocresol, b.p. 122—123°/26 mm. (*Hg* salt, m.p. 193—194°; corresponding disulphide, m.p. 65°). 2-Chloro-*m*-xylene-5-sulphonyl chloride, m.p. 121° (sulphonamide, m.p. 205°), similarly gives 4-chloro-3:5-dimethylthiophenol, b.p. 141—142°/29 mm. [*Hg* salt, m.p. 240—245° (decomp.); disulphide, m.p. 124—125°], whilst 2-chloro-*p*-xylene-5-sulphonyl chloride, m.p. 49—49.5° (sulphonamide, m.p. 189—190°), affords 4-chloro-2:5-dimethylthiophenol, m.p. 92.5° (disulphide, m.p. 103°). 2-Chloro-1-thiol-, m.p. 66.5° (disulphide, m.p. 134°), and 4-chloro-1-thiol-naphthalene, m.p. 51° (disulphide, m.p. 124—125°), are similarly prepared.

H. B.

Organic sulphides. C. LEFÈVRE and C. DESGREZ (Compt. rend., 1934, 198, 1432—1434).—The action of S at 140—200° on aliphatic acids is variable, but

aromatic amines and phenols are readily attacked, especially in presence of glycerol and a metallic carbonate, forming compounds of type $[\text{C}_6\text{H}_4(\text{NH}_2)\cdot\text{S}]_2$ and $[\text{C}_6\text{H}_4(\text{ONa})\cdot\text{S}]_2$. Di- and poly-phenols are still more readily attacked. At higher temp. monosulphides are formed.

E. W. W.

Synthesis of compounds related to the sterols, bile acids, and oestrogen-producing hormones. III. 7-Methoxy-1:2-cyclopentenophenanthrene, a dehydrogenation product of oestrin and equilenin. A. COHEN, J. W. COOK, C. L. HEWETT, and A. GIRARD (J.C.S., 1934, 653—658).—Interaction of equilenin (I) with *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ (II) in 10% KOH during 2.5 hr. at 100° affords the *Me* ether, m.p. 195.5—197.5°, the semicarbazone of which with NaOEt-EtOH at 180° during 20 hr. affords a demethylated product (a gum) which gives a *Me* ether (III), m.p. 121—122° (*picrate*, m.p. 128—129°). (III) is dehydrogenated by Se at 300—320° during 8 hr. to 7-methoxy-1:2-cyclopentenophenanthrene (IV), identical with the product prepared from oestrone (cf. this vol., 404), which suggests that dehydrogenation is accompanied by the loss of a quaternary Me. The diazonium derivative of α -naphthylamine-6-sulphonate with CuBr_2 in HBr (*d* 1.4) at 75—80° during 0.5 hr. affords *Na* 1-bromo-naphthalene-6-sulphonate, in which attempts to replace SO_3H also attacked Br. 5-Nitro- β -naphthylamine (A., 1892, 1232) is converted into 5-nitro- β -naphthol (A., 1923, i, 550), which with (II) in 10% KOH at 100° during 3 hr. affords 1-nitro-6-methoxynaphthalene, m.p. 74.5—75.5°, reduced (cf. A., 1925, i, 535) to 6-methoxy- α -naphthylamine (V), b.p. 190°/13—14 mm. (*Bz* derivative, m.p. 184—185°). (V) by the Sandmeyer or Gattermann reactions gives only very small (4%) yields of 1-bromo-6-methoxynaphthalene (*picrate*, m.p. 105—106°), but the 1-*I*-compound (VI), m.p. 33—33.5° (*picrate*, m.p. 98—99°), is formed in 45% yield. The Grignard derivative of (VI) with $(\text{CH}_2)_2\text{O}$ affords β -6-methoxy-1-naphthylethyl alcohol, b.p. 120—130°/0.2 mm. (3:5-dinitrobenzoate, m.p. 177.5—178°), converted by SOCl_2 into the chloride (VII), b.p. 160—165°/0.2 mm. (*picrate*, m.p. 74—76°). The Mg derivative of (VII) with 2-methylcyclopentanone in dry Et_2O at room temp. during 1 hr. affords α -di-(6-methoxy-1-naphthyl)butane, m.p. 150—150.5°, and a carbinol, b.p. 185—190°/0.15 mm., converted by KHSO_4 at 160—165° during 1 hr. into 1-(β -6'-methoxy-1'-naphthylethyl)-2-methyl- Δ^1 -cyclopentene, b.p. about 157°/0.15 mm. (*picrate*, m.p. 90—91°), which with AlCl_3 in CS_2 at 0° during 7 hr. affords 7-methoxy-1-methyl-1:2:3:4-tetrahydro-1:2-cyclopentenophenanthrene (VIII), a gum (*picrate*, m.p. 89.5—90°; *s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 110—110.5°), free from unwanted spirans (cf. A., 1933, 1042; this vol., 519). (VIII) with Se at 300—320° during 21.5 hr. affords 7-methoxy-1:2-cyclopentenophenanthrene, m.p. 136—137° (*picrate*, m.p. 136.5—137.5°; *s*- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ compound, m.p. 161—161.5°), identical with specimens obtained from oestrone and (I), but different from 1:2-cyclopentenophenanthrene. The ring system of oestrin and (I) is therefore the same as that of the sterols and bile acids, and OH is attached to the same position as the OH of cholesterol.

Ring I of œstrone and œstriol must be aromatic (cf. A., 1933, 605).

J. L. D.

Structure of œstrin. R. D. HAWORTH and G. SHELDRIK (Chem. and Ind., 1934, 431).—Synthetic 7-hydroxy-1:2-dimethylphenanthrene, m.p. 191—192° (OMe, m.p. 154°, OBz, m.p. 211°, derivatives), is identical with the dimethylphenanthrol obtained by the degradation of œstriol.

S. C.

Derivatives of *p*-xylocinol (β -orcinol). F. HENRICH, M. DANNEHL, H. HAERTLEIN, and W. HOFFMANN (J. pr. Chem., 1934, [ii], 140, 1—7).—With NaOH-EtOH and $C_6H_{11}ONO$, 2:6-dihydroxy-*p*-xylylene (β -orcinol) gives the *K* salt of its 3-NO-derivative (red and yellow forms), darkens 151°, m.p. 158°, which is obtained by acidification and is reduced by $SnCl_2-HCl$ to the 3-NH₂-compound, decomp. 198° (oxidised in air, but no definite products isolated), the hydrochloride of which with Ac_2O affords the O-Ac derivative, b.p. 275—280°, m.p. 101°, of 6-hydroxy-2:4:7-trimethylbenzoxazole, m.p. 175—176°, obtained by KOH-MeOH hydrolysis. With BzCl is similarly obtained 6-hydroxy-2-phenyl-4:7-dimethylbenzoxazole, sinters 185°, m.p. 187—188° (6-Bz derivative, b.p. 260°/15 mm., m.p. 142—143°).

J. W. B.

isoChavibetol. III. Oxidation of isochavibetol ethyl ether with potassium dichromate and hydrogen peroxide. M. IMOTO (J. Soc. Chem. Ind. Japan, 1934, 37, 117—118B).—*isoChavibetol* Et ether (I) with $K_2Cr_2O_7$ in dil. H_2SO_4 during 45 min. at 51—53° affords *isovanillin* Et ether, also formed from (I) with 3% H_2O_2 in $H_2O-FeSO_4$ during 15 min. at 51—53°.

J. L. D.

Substitution in 2-methoxy-nitrodiphenyl ethers. S. BUCHAN and H. A. SCARBOROUGH (J.C.S., 1934, 705—708).—4'-Nitro-2-methoxydiphenyl ether (I) with HBr (*d* 1.4) in boiling AcOH during 6 hr. affords the 2-OH-compound, m.p. 109°, and with $SnCl_2-HCl$ it gives 4'-amino-2-methoxydiphenyl ether, m.p. 97° [Ac derivative (II), m.p. 118°, nitrated at 15° to 3'-nitro-4'-acetamido-2-methoxydiphenyl ether (III), m.p. 124°, converted into the NH₂-compound (IV), m.p. 98°]. Deamination of (IV), or interaction of $m-C_6H_4I-NO_2$ with guaiacol (K salt) and Cu powder at 250° during 12 hr. gives 3'-nitro-2-methoxydiphenyl ether (V), m.p. 86°. (II) or (III) in HNO_3 (*d* 1.5) at 80° during 0.5 hr. affords 3':5-dinitro-4'-acetamido-2-methoxydiphenyl ether, m.p. 181° [NH₂-compound (VI), m.p. 163°]. Interaction of $m-C_6H_4I-NO_2$ with 5-nitroguaiacol (K salt) at 220°, the deamination of (VI), or (V) with HNO_3 during 2 hr., affords 3':5-dinitro-2-methoxydiphenyl ether, m.p. 123°; similarly prepared, 4':5-dinitro-2-methoxydiphenyl ether has m.p. 121° (OH-compound, m.p. 157°) and does not give a 4-substituted Br-compound. Interaction of $p-C_6H_4Cl-NO_2$ with 4-chloroguaiacol (K salt) at 220°, during 5 hr. affords 4-chloro-4'-nitro-2-methoxydiphenyl ether (VII), m.p. 104°, demethylated to the OH-compound, m.p. 121°. Similarly prepared, 4-bromo-4'-nitro-2-methoxydiphenyl ether (VIII) has m.p. 107°. Chlorination of (I) in AcOH, or interaction of (I) with SO_2Cl_2 at room temp., affords 5-chloro-4'-nitro-2-methoxydiphenyl ether (IX), m.p. 94° (which affords a NO_2 -derivative which does not react with piperidine

and hence has no 4-substituent), demethylated to the OH-compound, m.p. 94°, and reduced to 5-chloro-4'-amino-2-methoxydiphenyl ether, m.p. 90° [Ac derivative (X), m.p. 192°]. Similarly prepared Br-derivatives are: 5-bromo-4'-nitro-2-methoxydiphenyl ether (XI), m.p. 96°; OH-compound, m.p. 89°; 4'-NH₂- and NHAc-compounds (XII), m.p. 105° and 195°, respectively. Nitration of (X) in AcOH at 90° during 0.5 hr. affords 5-chloro-3'-nitro-4'-acetamido-2-methoxydiphenyl ether, m.p. 163° [base, m.p. 105°, deaminated to 5-chloro-3'-nitro-2-methoxydiphenyl ether (XIII), m.p. 85°, also formed from (V) with SO_2Cl_2 in Et_2O at 0°]. (I), (VII), or (IX) with Cl_2 in AcOH at room temp., or with excess of SO_2Cl_2 , or by interaction of $p-C_6H_4Cl-NO_2$ with 4:5-dichloroguaiacol (K salt) affords 4:5-dichloro-4'-nitro-2-methoxydiphenyl ether, m.p. 147° (further chlorinated to a Cl_3 -compound), demethylated to the OH-compound, m.p. 132° [also prepared by chlorinating the OH-derivatives of (I) and (IX)], and reduced to an amine, m.p. 122° [Ac derivative, m.p. 189°, which with HNO_3 (*d* 1.5) in AcOH at 80° affords 4:5-dichloro-3'-nitro-4'-acetamido-2-methoxydiphenyl ether, m.p. 164°, converted into the base, m.p. 174°, which is deaminated to 4:5-dichloro-3'-nitro-2-methoxydiphenyl ether, m.p. 123°, also obtained from (V) or (XIII) with Cl_2 in AcOH. (XII) with HNO_3 in AcOH at 90° affords 5-bromo-3'-nitro-4'-acetamido-2-methoxydiphenyl ether, m.p. 142° [base, m.p. 112°, deaminated to 5-bromo-3'-nitro-2-methoxydiphenyl ether (XIV), m.p. 93°, also obtained from (V) with Br in AcOH]. Interaction of $p-C_6H_4Cl-NO_2$ with 4:5-dibromoguaiacol (K salt), or bromination of (I), (VIII), or (XI) affords 4:5-dibromo-4'-nitro-2-methoxydiphenyl ether, m.p. 156° (not further brominated), demethylated to the OH-compound, m.p. 153° [also obtained from the OH-analogues of (I) and (XI) with Br in AcOH], and reduced to the amine, m.p. 106° [Ac derivative, m.p. 190°, nitrated in AcOH at 90° to 4:5-dibromo-3'-nitro-4'-acetamido-2-methoxydiphenyl ether, m.p. 165°, converted into the base, m.p. 179°, which is deaminated to 4:5-dibromo-3'-nitro-2-methoxydiphenyl ether, m.p. 131°, also obtained from (V) or (XIV) with Br in AcOH at 90° during 5 hr.].

J. L. D.

Analogues of tetryl. Hexanitrodiphenyl-aminoethyl nitrate. LE R. V. CLARK (Ind. Eng. Chem., 1934, 26, 554—556).—The explosive properties of β -di-2:4:6-trinitrophenylaminoethyl nitrate, m.p. 184° (corr.) (prepared in 80% yield from β -di-2:4-dinitrophenylaminoethyl alcohol and $H_2SO_4-HNO_3$), are recorded in detail. They compare favourably with those of other substances used as base charges in detonators.

R. S. C.

Preparation of *p*-dimethylaminobenzyl alcohol. L. H. SMITH and K. N. WELCH (J.C.S., 1934, 730).—Interaction of $NPhMe_2$, conc. HCl, and CH_2O at 37° during 48 hr. affords *p*-dimethylaminobenzyl alcohol, b.p. 125°/1 mm., identical with the product of Clemo and Smith (A., 1928, 1239), and 4:4'-tetramethyldiaminodiphenylmethane.

J. L. D.

Steric series. XXI. Validity of the rules of optical activity. K. FREUDENBERG and H. BILLER (Annalen, 1934, 510, 230—240).—(+)-Methyl-*n*-hexyl-, (+)-cyclohexylmethyl-, (I), $[M]_{589}^{25} + 7.5^\circ$ {acet-

ate, $[M]_{589}^{18}$ -5.4° ; carbomethoxy-derivative, b.p. $58^\circ/0.1$ mm., $[M]_{589}^{18}$ -6.1° [from (I) and ClCO_2Me in $\text{C}_5\text{H}_5\text{N}$ at $\gamma 5^\circ$]; nitrite, b.p. $56^\circ/9$ mm., $[M]_{589}^{18}$ -9.8° [from (I) and NOCl in $\text{C}_5\text{H}_5\text{N}$ at -15°], and (-)-phenylmethyl-carbinol, $[M]_{589}^{18}$ -51.6° [prepared by Houssa and Kenyon's method (A., 1930, 1576) (acetate, $[M]_{589}^{18}$ -192.8° ; carbomethoxy-derivative, b.p. $77^\circ/0.1$ mm., $[M]_{589}^{18}$ -169.7° ; nitrite, b.p. $33^\circ/0.1$ mm., $[M]_{589}^{18}$ -74.8°), *d*-mandelonitrile, $[M]_{589}^{20}$ $+62.1^\circ$ in hexane- Et_2O (4:1) [prepared by a slight modification of Smith's method (A., 1931, 483)], Me *d*-mandelate, *d*-mandeldimethylamide, Me *d*-atrolactate, and *d*-atrolactdimethylamide are all configurationally related. The effect of various groups on rotation is discussed briefly. The results of Levene and Meyer (this vol., 241) are attributed to a wrong application of the displacement rule, which demands large differences in the optical activity of similar compounds in order to settle questions of configuration. The validity of the vicinal rule cannot be taken for granted with compounds containing Ph groups (the contribution of which is liable to be affected by adjacent substituents). (I) is prepared by a modification of Domleo and Kenyon's method (A., 1926, 948) from *dl*-cyclohexylmethylcarbinol (benzoate, b.p. $132^\circ/2$ mm.) (improved prep. given; cf. Sabatier and Mailhe, A., 1904, i, 809). The benzoate of *dl*-CHPhMe-OH has b.p. $131^\circ/0.5$ mm.

H. B.

Formation of carbinols in condensation of aldehydes with hydrocarbons. F. D. CHATTAWAY and R. J. K. MUIR (J.C.S., 1934, 701—703).—Slow addition of C_6H_6 (1 mol.) to a vigorously shaken mixture of $\text{CCl}_3\text{CH}(\text{OH})_2$ (3 mols.) and conc. H_2SO_4 gives $\beta\beta\beta$ -trichloro- α -phenylethyl alcohol (I), b.p. $145^\circ/15$ mm., m.p. 37° (acetate, m.p. 87.5° ; benzoate, m.p. 97.5°) (cf. Dinesmann, A., 1905, i, 645), and $\text{CCl}_3\text{CHPh}_2$, m.p. 64° ; PhMe similarly affords $\beta\beta\beta$ -trichloro- α -*p*-tolylethyl alcohol (II), b.p. $155^\circ/13.5$ mm., m.p. 63° (acetate, m.p. 107.5° ; benzoate, m.p. 100.5°) (cf. *loc. cit.*), and $\beta\beta\beta$ -trichloro- $\alpha\alpha$ -*di-p*-tolylethane, m.p. 89° ; PhEt yields $\beta\beta\beta$ -trichloro- α -*p*-ethylphenylethyl alcohol, b.p. $175^\circ/25$ mm.; PhI furnishes $\beta\beta\beta$ -trichloro- $\alpha\alpha$ -*di-p*-iodophenylethane, m.p. 172° (a carbinol could not be isolated). (I), PhMe (> 1 mol.), and conc. H_2SO_4 give $\beta\beta\beta$ -trichloro- α -phenyl- α -*p*-tolylethane (III), m.p. 72.5° , also prepared similarly from (II) and C_6H_6 . The following are similarly prepared: $\beta\beta\beta$ -trichloro- α -phenyl- α -*p*-chloro-, m.p. 74° , -*p*-bromo-, m.p. 96° , and -*p*-iodo-phenylethane, m.p. 119.5° ; $\beta\beta\beta$ -trichloro- α -*p*-chloro-, m.p. 81° , -*p*-bromo-, m.p. 102° , and -*p*-iodo-, m.p. 117° , -phenyl- α -*p*-tolylethane. (III) and conc. EtOH-KOH give $\beta\beta$ -dichloro- α -phenyl- α -*p*-tolylethylene, m.p. 87.5° . $\beta\beta$ -Dichloro- α -phenyl- α -*p*-chloro-, m.p. 93° , -*p*-bromo-, m.p. 113° , and -*p*-iodo-phenylethylene, m.p. 108° , and $\beta\beta$ -dichloro- α -*p*-iodo-phenyl- α -*p*-tolylethylene, m.p. 90° , are similarly prepared.

H. B.

Steric series. XX. Configuration of ephedrine. K. FREUDENBERG and F. NIKOLAI (Annalen, 1934, 510, 223—230; cf. A., 1932, 267).—*d*-(+)- α -Dimethylaminopropiondimethylamide (I), b.p. 83 — $84^\circ/12$ mm., $[\alpha]_{578}^{18}$ $+17.9^\circ$ [the *dl*-form (*picrate*, m.p. 127 — 128°) has the same b.p.], prepared from *l*-(+)- α -

chloropropiondimethylamide (A., 1930, 1556) and $\text{Et}_2\text{O-NHMe}_2$ at 20° , gives a (+)-methiodide, m.p. 190 — 191° (the *dl*-form has m.p. 172 — 173°), $[\alpha]_{578}^{18}$ $+35.4^\circ$ in H_2O . Reduction (H_2 , Pt-black, H_2O) of the (+)-dimethylamide of *l*-(+)- α -azidopropionic acid gives the (+)-dimethylamide, b.p. 64 — $66^\circ/0.5$ mm., $[\alpha]_{578}^{18}$ $+14.6^\circ$, of *l*-(+)-alanine, which with EtOH-Mel and subsequent treatment with TIOEt affords the (-)-methiodide, $[\alpha]_{578}^{18}$ -15.4° in H_2O , of *l*-(+)- α -dimethylaminopropiondimethylamide. (I) and MgPhBr give (+)- α -dimethylamino- α -benzoylthane, b.p. 115 — $117^\circ/11$ mm., $[\alpha]_{578}^{18}$ $+24.9^\circ$ [the *dl*-form (II) (*picrate*, m.p. 134 — 135°) has the same b.p.], which is reduced (H_2 , Pt-black, $2N\text{-HCl}$) to a mixture (A), b.p. 122 — $124^\circ/10$ mm., $[\alpha]_{578}^{18}$ $+14.21^\circ$, of *d*-methylephedrine and *l*-methyl- ψ -ephedrine; (II) similarly affords a mixture (Bz derivative, b.p. 138 — $140^\circ/0.1$ mm.) which with picric acid gives *dl*-methyl- ψ -ephedrine *picrate*, m.p. 148 — 149° . Natural (-)-ephedrine (III) is converted by Schmidt's method (A., 1914, i, 989) into (+)- β -methylamino- α -phenylpropane hydrochloride, m.p. 172° , $[\alpha]_{578}^{18}$ $+21.6^\circ$ in H_2O (free base, b.p. 88 — $89^\circ/12$ mm.), which with Mel and TIOEt gives the (-)-methiodide, m.p. 204 — 205° , $[\alpha]_{578}^{18}$ -32.89° in H_2O , of β -dimethylamino- α -phenylpropane; (A) similarly affords the (+)-methiodide, m.p. 198 — 199° , $[\alpha]_{578}^{18}$ $+39.65^\circ$ in H_2O . The results show that (III) is configurationally related to natural *l*-(+)-alanine (cf. Leithe, A., 1932, 627). *dl*- α -Aminopropiondimethylamide *picrate* has m.p. 203 — 204° .

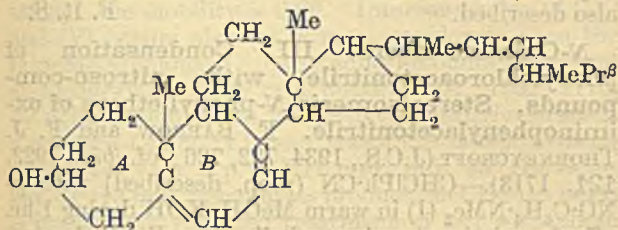
H. B.

Condensation of oleyl acetate with aromatic hydrocarbons. J. P. SISLEY (Chim. et Ind., 1934, 31, Spec. No., 763—764).—Oleyl acetate, b.p. 152 — $153^\circ/33$ mm., from oleyl alcohol, Ac_2O , and conc. H_2SO_4 , with AlCl_3 and C_6H_6 at 35 — 65° affords phenylstearyl acetate, b.p. 188 — $190^\circ/33$ mm., hydrolysed by KOH-EtOH to phenylstearyl alcohol (I), b.p. 175 — $180^\circ/28$ mm.; indications of the presence of a solid isomeride of (I) are obtained.

H. W.

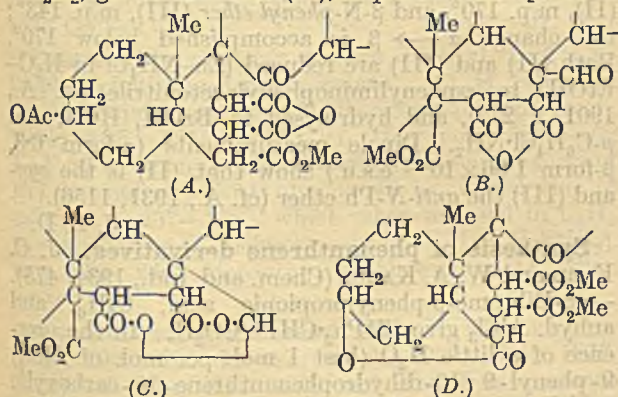
Constitution of ergosterol. A. WINDAUS, H. H. INHOFFEN, and S. VON REICHEL (Annalen, 1934, 510, 248—259).—Ergostanetriol (I), m.p. 247 — 248° [the diacetate, m.p. 190° , $[\alpha]_{578}^{18}$ $+6.5^\circ$ (all rotations are in CHCl_3), is prepared by reduction of ergostenetriol diacetate B, m.p. 210 — 211° , $[\alpha]_{578}^{18}$ $+25.9^\circ$ (Heilbron *et al.*, A., 1933, 500)], consumes 10 when oxidised with $\text{Pb}(\text{OAc})_4$ in AcOH , thus showing that the two new OH groups in ergostadienetriol (A., 1930, 1178) are adjacent. Since one of these OH groups is *sec.* and the other *tert.*, the structure previously proposed (this vol., 186) for ergosterol (II) is excluded. (I) is oxidised (CrO_3 , AcOH) to ergostanoldione, m.p. 262° (decomp.), $[\alpha]_{578}^{18}$ -26.6° , dehydrated by HCl in CHCl_3 to ergostenedione (III), m.p. 156° , $[\alpha]_{578}^{18}$ -51.4° [enol Et ether (IV), m.p. 161°], which is reduced (Zn dust, AcOH) to ergostanedione, m.p. 199° , $[\alpha]_{578}^{18}$ -2.9° [pyridazine derivative, m.p. 210° (decomp.) (sinters at 190°), formed with $\text{EtOH-N}_2\text{H}_4\text{H}_2\text{O}$]. (III) has the same absorption spectrum as cholestenedione (V) (cf. A., 1906, i, 580; 1907, i, 212) and stigmastadienedione (Fernholz, this vol., 292), whilst (IV) shows the same spectrum as the enol Et ether of (V). The group $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}\cdot\dot{\text{C}}\cdot\text{CO}\cdot$ is, therefore, common to

both (III) and (V) and indicates that the OH group of (II) is on C₃. The chloroallocholic acid of Heilbron *et al.* (A., 1933, 1290) is considered to be a stereoisomeride of 3-chloroallocholic acid. The following constitution is now assigned to (II).



It is reported that neoergosterol must contain three double linkings in ring B, since it is dehydrogenated (Pt-black) to a phenol, C₂₇H₃₆O, in which ring A is aromatic also. H. B.

Ozonisation of 22 : 23-dihydroergosteryl acetate-maleic anhydride. A. WINDAUS and H. H. INHOFFEN (Annalen, 1934, 510, 260—268).—Fission of the ozonide (I) of 22 : 23-dihydroergosteryl acetate-maleic anhydride with boiling AcOH or CrO₃-AcOH at 100° (bath) and subsequent esterification (Et₂O-CH₂N₂) give a *Me* ester (II), m.p. 307—308° [as *A* or



B (or *C*); remainder of mol. as in dihydroergosterol], which when hydrolysed (MeOH-KOH) and then treated with Me₂SO₄ affords the Me₂ ester lactone, m.p. 237—238° (as *D* or *E*). Hydrolysis (MeOH-conc. HCl) of (II) gives an amorphous ester [acetylated to (II)], oxidised (CrO₃, AcOH) to the *keto*-derivative, m.p. 244—245° (as *A*, *B*, or *C* with CH-OAc=CO). Reduc-

tive fission (Zn dust, AcOH, Et₂O or H₂, Pt, AcOH-EtOAc) of (I) and subsequent esterification (CH₂N₂) gives a *Me* ester, m.p. 253—254° (? as *B*, with CHO=CH₂·OH) (*Ac* derivative, m.p. 238—239°), which is oxidised (CrO₃, AcOH) to (II). The above alternative structures are based on the old (this vol., 186) and new (preceding abstract) structures for ergosterol. It is possible that the formation of the maleic anhydride adduct involves an isomerisation, but the ready thermal decomp. of the adducts (regenerating the original products) suggests that this is improbable. H. B.

Constitution of ergosterol. J. W. COOK and G. A. D. HASLEWOOD (Chem. and Ind., 1934, 507—508).—Neoergosterol (I) and KHSO₄ at 145—150° in CO₂ give *neorgostapentaene* (II), C₂₇H₃₈, m.p. 93—94°, [α]_D²⁰ +51° in EtOH, also obtained (contaminated with a trace of a Cl-compound) from (I) and SOCl₂ in NPhMe₃. (II) could not be reduced by Na and EtOH or amyl alcohol, indicating that if ring II is aromatic then the double linking in ring I is not C₃:C₄. (II) is also unaffected by boiling 20% NaOEt, indicating that the double linking of ring I is not C₂:C₃. These results are difficult to reconcile with the structure proposed by Windaus *et al.* (see above) for ergosterol. H. B.

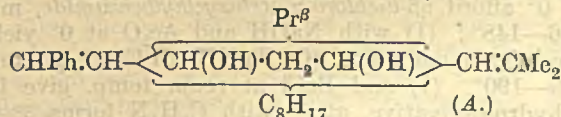
Colloidal condition of cholesterol, cholesteryl ester, and lecithin. IX. Nature of catalysis by cholesterol.—See this vol., 606.

So-called "law of periodicity." A. HANTZSCH and A. BURAWOY (Ber., 1934, 67, [B], 788—792).—Mainly in reply to the criticisms by Petrenko-Kritschenko (this vol., 186) of the authors' conception of triarylmethyl compounds (A., 1933, 1158), it is pointed out that periodicity is observed only in the behaviour of the Cl-compounds of CH₄ towards the strongest bases. A general law of periodicity does not exist. The absorption of the triarylmethyl ion does not change periodically with the no. of positive groups. H. W.

Valency isomerism of derivatives of triarylmethanes. A. HANTZSCH and A. BURAWOY (Ber., 1934, 67, [B], 793—798).—A reply to Lifschitz (A., 1933, 1104). H. W.

Relative reaction velocities of alcohols with phenylcarbimide.—See this vol., 604.

Onocerin, the phytosterol of *Ononis spinosa*, L. H. DIETERLE and A. SALOMON (Arch. Pharm., 1934, 272, 142—151).—Degradation products of onocerin (I), C₂₆H₄₄O₂, m.p. 232°, [α]_D²⁰ +12.05° in CHCl₃ (cf. Thoms, A., 1897, i, 201; Hemmelmayr, A., 1906, i, 356; 1907, i, 184), have now been obtained cryst. With CrO₃-AcOH (I) gives onoceric acid (II) and *onodiketone*, C₂₆H₄₀O₂, m.p. 189° (*bisdinitrophenylhydrazone*, m.p. 206—207°), and with fuming HNO₃ it affords *dinitro-onoceric acid*, sinters 146°, decomp. 184°, also obtained from HNO₃ and (II). Oxidation of (I) with O₃ in AcOH gives *dioxynodiketone*, C₂₆H₄₄O₄, m.p. 211° (*bisdinitrophenylhydrazone*, m.p. 227°), which with CrO₃ gives COMe₂ and a *ketone*, C₁₂H₂₄O, m.p. 90—91° (*dinitrophenylhydrazone*, m.p. 175—176°), further oxidised by alkaline KMnO₄ to an *acid* (III), C₇H₁₂O₄ (*Ag* salt), and COMe₂. Ozonolysis of (I) affords COMe₂, PhCHO, and a *keto-acid*, C₁₀H₁₈O₃, m.p. 150—151° (*dinitrophenylhydrazone*, m.p. 165—166°), further oxidised to (III). The presence of two double linkings in (I) is shown by the formation of a Br₄-derivative, m.p. 76—77°, titration with BzO₂H, and reduction (PtO₂-H₂-AcOH) to a



tetrahydro-derivative. The partial formula (A) is assigned to (I). J. W. B.

Relations between acidity and tautomerism. II. Amide group, hydroxamic, sulphinic, and sulphydroxamic acids. F. ARNDT and H. SCHOLZ (Annalen, 1934, 510, 62—71; cf. A., 1933, 146).—Saccharin (I) in Et₂O and Et₂O-CH₂N₂ (II) give [in agreement with Heller (A., 1925, i, 1323)] *O*- (III) and *N*- (IV) -Me derivatives in the ratio 1 : 4. Addition of solid (I) to (II) affords [in agreement with Schönberg *et al.* (A., 1933, 291)] essentially (IV). In the former case, the amount of (III) depends on the conversion (in solution) of the NH- into the OH-form. Phthalimide does not react with (II) except in presence of H₂O or MeOH; the *N*-Me derivative is the main product with MeOH-(II), but a small amount of a OMe-containing compound is also produced. Benzhydroxamic acid reacts as OH·CPh·N·OH with (II) to give (mainly) OMe·CPh·N·OMe, b.p. 105—106°/13 mm.; the compound, $\text{CPh} \begin{matrix} \text{N} \\ \diagup \\ \text{NPh} \cdot \text{CO} \end{matrix}$ m.p. 170° (lit. 167°), is formed as a by-product (probably by elimination of MeOH from the intermediate OMe·CPh·N·OH, subsequent isomerisation of the PhCNO to PhNCO, and the interaction of these compounds). *p*-C₆H₄Me·SO₂H (V) and (II) afford (mainly) the Me ester of (V) and no *p*-tolyl Me sulphone, indicating that the H of (V) is not attached to S. *p*-Toluenesulphydroxamic acid and an excess of (II) give some *p*-C₆H₄Me·SO₂Me and (mainly) the ester, *p*-C₆H₄Me·SO₂·NMe·OMe, m.p. 57°, which is stable to conc. HCl and Zn-AcOH or Zn-EtOH-HCl, thus emphasising the difference (cf. *loc. cit.*) between CO and SO₂ groups. H. B.

Di-β-bromoallylaminoethyl *p*-aminobenzoate. W. BRAKER and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1934, 23, 322—324).—*Di-β-bromoallylaminoethyl alcohol*, b.p. 141—145°/9—10 mm. (prepared in 66% yield by condensing βγ-dibromo-Δ^α-propylene with aminoethyl alcohol in presence of Ag₂O), in C₆H₆ solution was refluxed with *p*-aminobenzoyl chloride to yield the dihydrochloride of *di-β-bromoallylaminoethyl p-aminobenzoate* (I), a yellow oil. (I), in aq. solution, is too acid for anaesthetic tests. Buffering ppts. the base from solution. A. E. O.

Constitution of the reduction products of chloral and bromal amides. B. H. YELBURG and T. S. WHEELER (J. Indian Chem. Soc., 1934, 11, 217—223).—ββ-Dichlorovinylbenzamide, obtained by reducing chloralbenzamide with Zn-AcOH, with Br in CHCl₃ and subsequent hydrolysis with H₂O gives ββ-dichloro-β-bromo-α-hydroxy-, m.p. 128—130°, and with HCl or HBr followed by Na₂CO₃, forms ββ-dichloro-α-hydroxy- (I), m.p. 118—119°, which with PCl₅ yields αββ-trichloro- (II), m.p. 102—103°, and with PBr₅, ββ-dichloro-α-bromo-ethylbenzamide, b.p. 158°/8 mm. (II) and NH₂Ph in NMe₂Ph give ββ-dichloro-α-anilinoethylbenzamide, m.p. 190—192°. (I) and Ac₂O at the b.p. form ββ-dichlorovinylbenzamide, and at 0° afford ββ-dichloro-α-acetoxyethylbenzamide, m.p. 146—148°; (I) with NaOH and Ac₂O at 0° yields the anhydro-compound (CPh·NH·CH·CHCl₂)₂O, m.p. 189—190°. (I) and BzCl at room temp. give the anhydro-derivative, at 0° with C₅H₅N forms ββ-dichloro-α-benzoyloxy-, m.p. 131°, and with NaOH-Me₂SO₄, ββ-dichloro-α-methoxy-ethylbenzamide, m.p.

99—100°. ββ-Dichloro-α-hydroxyethyl-acetamide, m.p. 118—119°, and -propionamide, m.p. 116°; ββ-dibromovinylbenzamide, m.p. 75°; ββ-dibromo-α-hydroxyethylbenzamide, m.p. 130°, its anhydro-, m.p. 162°, OAc-, m.p. 138°, and O-Me derivative, m.p. 124—126°, are also described. F. R. S.

N-Oximino-ethers. III. Condensation of phenylchloroacetonitrile with nitroso-compounds. Stereoisomeric N-phenyl ethers of oximinophenylacetonitrile. F. BARROW and F. J. THORNEYCROFT (J.C.S., 1934, 722, 726; cf. *ibid.*, 1922, 121, 1713).—CHClPh·CN (prep. described) with *p*-NO·C₆H₄·NMe₂ (I) in warm MeOH-KOH during 1 hr. afford oximinophenylacetonitrile *N-p*-dimethylamino-phenyl ether, m.p. 185°, hydrolysed (25% HCl at 100°) to BzCN, (I), and *p*-NH₂·C₆H₄·NMe₂ (*p*-nitrobenzoate, m.p. 258°). The following are also described: oximinophenylacetonitrile *N-p*-methylaminophenyl ether, m.p. 193°; *N-p*-diethylamino-, m.p. 153°; *N-p*-ethylamino-, m.p. 185°; *N-p*-benzylethylamino-, m.p. 142°; *N-p*-phenylamino-, m.p. 154°, and *N-p*-amino-phenyl ether, m.p. 195°. None of these compounds can be obtained in stereoisomeric forms. CHClPh·CN with PhNO in KOH during 45 min. at 30° affords a mixture of α- and β-ethers, separated by C₆H₆ into the α- (II), m.p. 170°, and β-*N*-phenyl ether (III), m.p. 143°; the change α → β is accomplished below 170°. Both (II) and (III) are reduced (Zn-NH₄Cl in H₂O-EtOH) to α-phenyliminophenylacetonitrile (cf. A., 1901, i, 272), and hydrolysed to BzOH, HCN, and *p*-C₆H₄Cl·NH₂. Dipole measurements (α-form 6.3, β-form 1.06 × 10⁻¹⁸ e.s.u.) show that (II) is the *syn*- and (III) the *anti-N*-Ph ether (cf. A., 1931, 1156). J. L. D.

Synthesis of phenanthrene derivatives. J. C. EARL and W. A. KABLE (Chem. and Ind., 1934, 475).—αβ-Dibromo-β-phenylpropionic acid, C₆H₆, and anhyd. AlCl₃ give CHPh₂·CHPh·CO₂H. In the presence of a little H₂O (best 1 mol. per mol. of AlCl₃) 9-phenyl-9 : 10-dihydrophenanthrene-10-carboxylic acid is formed (cf. A., 1932, 382). R. S. C.

Olefinic acids. XII. β-Phenylhexenoic and β-methylpentenoic acids. G. A. R. KON, R. P. LINSTAD, and J. M. WRIGHT (J.C.S., 1934, 599—604).—β-Phenyl-Δ^β-hexenoic acid (I), b.p. 154—156°/3 mm. (Et ester, b.p. 153—155°/22 mm.), is obtained by hydrolysis (cold aq. EtOH-KOH) of the crude Et ester (A., 1926, 1245) and partial esterification (method : A., 1930, 1582) of the resulting acid. Equilibrium between *cis*- (II) or *trans*- (III) -β-phenyl-Δ^β-hexenoic acid (Stoermer *et al.*, A., 1917, i, 647; *loc. cit.*) and (I) is established slowly with boiling alkali; the equilibrium mixture contains 32% of αβ-form and the mobility [(k₁ + k₂) × 10] is 0.05—0.1. Each acid appears to give a mixture of all three; interconversion of (II) and (III) is incomplete and very slow, and the nature of the equilibrium (if any) between (II) and (III) could not, therefore, be determined. The amount of (I) in mixtures of (I), (II), and (III) can be determined by a bromometric method; an approx. separation of (II) and (III) is effected through their basic Cu salts. β-Methyl-Δ^α-pentenoic acid (A., 1925, i, 506) is separated into a *trans*- (IV), m.p. 48—49° (chloride, b.p. 85—86°/20 mm.; amide, m.p. 94—

94.5°) (cf. *loc. cit.*), and a *cis-form* (V), b.p. 96°/5 mm., m.p. 12° [which gives the same derivatives as (IV)]. Equilibration of (IV) or (V) gives mixtures containing 62.5% of *cis*- β -methyl- Δ^{α} -pentenoic acid (VI), b.p. 90—94°/7 mm., m.p. 1° (separated by partial esterification); the mobility is 0.69. Interconversion of (IV) and (V) occurs also (at a more rapid rate than the tautomeric change); approx. equal amounts are present at equilibrium. The acid obtained (A., 1932, 1110) by dehydration of Et β -hydroxy- β -methylvalerate is a mixture (A) of (VI) and trans(?) β -methyl- Δ^{β} -pentenoic acid (VII), b.p. 95°/11 mm., m.p. 35° [Et ester, b.p. 63°/13 mm. (ozonolysis product, MeCHO)]; (VII) is isolated by repeated treatment of (A) with alkali followed by partial esterification. (VII) does not appear to participate in the tautomeric interchange in presence of alkali. (IV), (V), and (VI) are converted by cold conc. H₂SO₄ into β -methyl- γ -valerolactone (VIII) at approx. the same rate; the change $\alpha\beta \rightleftharpoons \beta\gamma$ -acid must, therefore, be more rapid than lactonisation. In agreement with this view, the $\alpha\beta$ -acid can be isolated from the product of incomplete lactonisation of (VI). β -Hydroxy- β -methylvaleric acid also accompanies (VIII); this is not an intermediate since it is converted by cold conc. H₂SO₄ into (VIII) (and the unsaturated acids) at a much slower rate than (IV)—(VI). H. B.

Dissociable organic oxides. Ethyl 1:1':3'-triphenylrubene-3-carboxylate, C₃₆H₂₃·CO₂Et; its dissociable oxide. M. BADOCHÉ (Compt. rend., 1934, 198, 1515—1518; cf. this vol., 523).—Ag 1:1':3'-triphenylrubene-3-carboxylate and excess of EtI in cold dry Et₂O during 48 hr. afford the Et ester, m.p. 237—238°, which when exposed in C₆H₆ to sunlight and O₂ yields a peroxide, C₃₆H₂₃·CO₂Et[O₂], m.p. 239—240° (decomp.), which evolves O₂ when heated. J. L. D.

Asymmetric syntheses. III. R. WEGLER (Annalen, 1934, 510, 72—87; cf. A., 1932, 1094; 1933, 1139).—*dl*-OAc·CHPh·COCl and MeOH in presence of CCl₄ (or CHCl₃) and a small amount of brucine (I) at 40° give (usually) a (+)-ester (not homogeneous); increase in the quantity of (I) affords an ester which is (−) [or slightly (+)]. CHPhCl·COCl and OMe·CHPh·COCl similarly give (−)-esters, irrespective of the amount of (I) used. CHRPh·COCl (R = Et, Pr, Bu) give (−)- and (+)-esters with small and large amounts, respectively, of (I). With CHEtPh·COCl + BzCl and (I), a (−)-ester is obtained. The probable course of the reaction is discussed. (−)-CHPhEt·OH and HCl at −8° give an almost inactive chloride; in presence of brucine hydrochloride (II), the racemisation is largely suppressed. *dl*-(II), the racemisation is largely suppressed. *dl*-CHPhEt·OH and HCl in CCl₄ + (II) give CHPhEtCl of varying rotation, according to the conditions [temp.; amount of (II)] used. Selective adsorption of the alcohol by (II) probably occurs. The original must be consulted for details. H. B.

Synthesis of Δ^1 - and Δ^2 -cyclopentene-1:2-dicarboxylic acids. B. L. NANDI (J. Indian Chem. Soc., 1934, 11, 213—216).—Et cyclopentan-1-one-2-carboxylate gives with HCN the corresponding -1-hydroxy-1-cyano-ester, dehydrated (SOCl₂-C₆H₅N) to Et 1-cyanocyclopentene-2-carboxylate, b.p. 132°/

11 mm., which is hydrolysed to a mixture of Δ^1 -, m.p. 178°, and Δ^2 -cyclopentene-1:2-dicarboxylic acid, m.p. 146°, identified by ozonolysis. Attempts to follow the equilibration of the two acids were not successful. F. R. S.

Synthesis of Δ^2 -cyclopentene-1:3-dicarboxylic acid. Relation to glutaconic acid derivatives. B. L. NANDI (J. Indian Chem. Soc., 1934, 11, 277—281).—Et butane- $\alpha\alpha\delta\delta$ -tetracarboxylate (J.C.S., 1894, 65, 578) is cyclised by NaOEt in boiling EtOH during 3 hr. to Et cyclopentanone-2:5-dicarboxylate, b.p. 169—175°/5 mm., reduced (H₂-Pt) to Et cyclopentanol-2:5-dicarboxylate, b.p. 173—175°/27 mm., dehydrated by SOCl₂ in cold C₅H₅N during 12 hr. to Et Δ^2 -cyclopentene-1:3-dicarboxylate (I), b.p. 168°/21 mm., which is hydrolysed (NaOH-EtOH) at room temp. to the acid, m.p. 150.5°. Et Δ^1 -cyclopentene-1:3-dicarboxylate (A., 1932, 1127) does not react with Et₂C₂O₄ in PhMe or C₆H₆ containing Na or K (cf. J.C.S., 1901, 79, 1265). The sodio derivative of (I) with MeI in boiling C₆H₆ during 1 hr. affords a methylated ester, hydrolysed to an acid, m.p. 225° (decomp.), which is stable to 20% KOH and affords neither a neutral nor an enolic anhydride. This confirms previous observations (A., 1932, 1127) that tautomerism and stereoisomerism are independent of one another in the glutaconic acids. J. L. D.

Preparation of ammonium phthalate. C. L. TSENG and M. HU (Sci. Quart. Nat. Univ. Peking, 1934, 4, 237—242).—The action of dry NH₃ on phthalic acid in EtOH yields *o*-C₆H₄(CO₂NH₂)₂, m.p. 199°. W. R. B.

Condensation of *o*-2-fluorenylbenzoic acid. A. DANSI and A. SEMPRONJ (Gazzetta, 1934, 64, 218—221; cf. this vol., 78).—*o*-2-Fluorenonoylbenzoic acid (I) has m.p. 259—260° (not 248—250°, cf. A., 1904, i, 168) and is identical with the acid described as phenylanthraquinonecarboxylic acid (this vol., 78). At above 370°, it undergoes carboxyl-scission, yielding 2-benzoylfluorenone, m.p. 175—177° (cf. Fortner, A., 1903, i, 177). When, however, the acid is heated at 360—365°, ring-closure occurs, with formation of 2:3-benzoyleneanthraquinone, m.p. 351° (cf. Ullmann and Gupta, A., 1914, i, 413). The course followed by the condensation of (I) cannot be determined, but it seems probable that the CH₂ of the fluorene also takes part and that the product is not a phthaloylfluorene, but a compound of high mol. wt. T. H. P.

Preparation of homopiperonylic acid. T. S. STEVENS (J. pr. Chem., 1934, [ii], 140, 46).—The modification of Slotta *et al.* (this vol., 407) is best for the prep. of the methylenedioxy mandelate, but the author's earlier procedure (A., 1927, 265) for its reduction is recommended. J. W. B.

Synthesis of dicyclic compounds. P. C. GUHA, K. N. GAIND, and D. R. MEHTA (Current Sci., 1933, 2, 53).—The Na₂ derivative of Et₂ 4:6-diketo-2:2-dimethylcyclohexane-1:3-dicarboxylate in C₆H₆ reacts at a high temp. in a closed vessel with CH₂I₂, with subsequent hydrolysis, to give ketonopinone. Succinosuccinic ester similarly affords the 1:4-bridged compound. CH. ABS.

Attempts to synthesise cantharidin. V. N. PAI and P. C. GUHA (J. Indian Chem. Soc., 1934, 11, 231—237).—Me cyclohexane-3 : 6-dione-1 : 2-carboxylate (improved prep.) with NaOMe in MeOH-MeI gives the 2-C-Me derivative (I), m.p. 91—93° (cf. Helferich, A., 1921, i, 185), whilst with NaOH-Me₂SO₄ it forms Me 3 : 6-dimethoxy-4 : 5-dihydrophthalate, b.p. 140—143°/1 mm., hydrolysed with KOH-EtOH to succinic acid and with H₂SO₄ to 1 : 4-diketocyclohexane. The K derivative of (I) and MeI forms a mixture of the C-Me₂ and C-methyl-O-methoxy-derivatives.

F. R. S.

Preparation of ethyl α -isobutyryl- β -phenylpropane- $\alpha\gamma\gamma$ -tricarboxylate. Retrogression of the Michael reaction. E. H. KROEKER and S. M. McELVAIN (J. Amer. Chem. Soc., 1934, 56, 1171—1173).—isoButyrylacetonitrile, b.p. 102—104°/12—13 mm. (from PrⁿCO₂Et, MeCN, and NaOEt at 115—120°), is hydrolysed (EtOH-HCl and H₂O) to Et isobutyrylacetate (I), b.p. 90—92°/15—16 mm., which with PhCHO and piperidine at -5° to room temp. gives Et α -isobutyrylcinnamate (II), b.p. 148—153°/3 mm. The amounts of Et α -isobutyryl- β -phenylpropane- $\alpha\gamma\gamma$ -tricarboxylate, b.p. 188—190°/3 mm., (I), CH₂(CO₂Et)₂ (III), and (II)+CHPh.C(CO₂Et)₂ (IV) obtained under varying conditions from equimol. amounts of (I) and (IV) and of (II) and (III) in Et₂O containing a little NaOEt are determined; some Et β -phenylpropane- $\alpha\gamma\gamma$ -tetracarboxylate [from (III) and (IV)] is probably formed also. (II) and (III) are best used in the above synthesis.

H. B.

Structures of olivil and its derivatives. B. L. VANZETTI (Atti R. Accad. Lincei, 1934, [vi], 19, 421—424; cf. A., 1912, i, 352; 1931, 226).—The "difficultly sol. acid" obtained by oxidation of methylisoolivil is shown to be 2-(3' : 4'-dimethoxybenzoyl)-4 : 5-dimethoxybenzoic acid, and the "neutral substance," obtained at the same time, the corresponding phthalide. A mechanism is suggested for the conversion of olivil into isoolivil. Experimental data are to be published later. T. H. P.

Reduction products of Δ^1 -cyclopentene-1-aldehyde. E. URION (Compt. rend., 1934, 198, 1518—1520; cf. A., 1930, 1039).—Reduction (H₂-Pd) of Δ^1 -cyclopentene-1-aldehyde (I) affords cyclopentane-aldehyde (this vol., 389), whereas with Zn-Cu in AcOH it affords Δ^1 -cyclopentenylcarbinol, b.p. 66°/11 mm. [*phenylurethane*, m.p. 64—65°; *H phthalate*, m.p. 234° (decomp.)], and $\alpha\beta$ -di- Δ^1 -cyclopentylethylene glycol, m.p. 123° (*Bz*₂ derivative, m.p. 127°), reduced (H₂-Pd) to $\alpha\beta$ -dicyclopentylethylene glycol, m.p. 133°.

J. L. D.

Nitration of chloro-*p*-xylene. H. WAHL (Compt. rend., 1934, 198, 1612—1615).—Nitration of chloro-*p*-xylene by H₂SO₄-HNO₃ is accompanied by oxidation to 3-chloro-*p*-toluic acid (I), 3-chloro-*p*-tolualdehyde (II), b.p. 115—118°/15 mm., m.p. 30° [oxime, m.p. 95°; phenylhydrazone, m.p. 118°; semicarbazone, m.p. 230° (decomp.)]; NaHSO₃ compound. M.p. are corr., and another aldehyde, b.p. about 160°/15 mm. (II) with 50% KOH gives (I) and 3-chloro-4-methylbenzyl alcohol, b.p. 135—136°/15 mm., m.p. 29°.

R. S. C.

Cannizzaro reaction.—See this vol., 604.

Effect of the nitro-group in three-carbon tautomerism. H. B. FRASER and G. A. R. KOX (J.C.S., 1934, 604—610).—cycloHexanone (I) and MeNO₂ in EtOH-NaOEt give 1-nitromethylcyclohexanol (II), b.p. 125—130°/17 mm., dehydrated (best with SOCl₂ in cold C₅H₅N) to 1-nitromethyl- Δ^1 -cyclohexene (III), b.p. 106—108°/17 mm.; condensation with piperidine (usual method) leads to a mixture of (II) and (III). (III) and O₃ in EtOAc give a stable ozonide, m.p. 105°, decomposed by aq. 10% NaHCO₃ to adipic acid (IV), which is also formed by oxidation (aq. KMnO₄) of (III). (III) can be titrated fairly rapidly with alkali in EtOH (end-point not sharp) and its dil. aq. solution is acidic (litmus); freshly prepared solutions do not give a colour with FeCl₃. (III) and NaOEt in Et₂O give a Na derivative (V), which dissolves in H₂O to an alkaline solution (this develops a purple colour with FeCl₃); cautious acidification affords the *aci*-form, m.p. 63—65°, which is sol. in aq. NaHCO₃, gives a colour with FeCl₃, and rearranges fairly rapidly to (III). (V) is unaffected by MeI or EtI in C₆H₆ or Et₂O, but in EtOH Δ^1 -tetrahydrobenzaloxime, m.p. 98°, results (cf. Kohler and Stone, A., 1930, 464); these results show that the anionic charge in the nitrolate ion remains throughout on O and that there is no tendency for its redistribution even to C₃ of the three-carbon system. Rearrangement of the *aci*- to the NO₂-form does not involve the three-carbon system. (III) and NH₃ in Et₂O give an NH₄ salt, which decomposes in a vac. desiccator regenerating (III), and develops a brilliant green colour when treated with dil. HCl in Et₂O. (I) and EtNO₂ afford 1- α -nitroethylcyclohexanol, b.p. 122—125°/14 mm., dehydrated (as above) to 1- α -nitroethyl- Δ^1 -cyclohexene, b.p. 120—123°/24 mm. [oxidised (KMnO₄ or O₃) to (IV) and AcOH], whilst (I) and PrⁿNO₂ give 1- α -nitropropylcyclohexanol, b.p. 140—145°/12 mm., dehydrated to 1- α -nitropropyl- Δ^1 -cyclohexene, b.p. 117—118°/11 mm. [oxidised (KMnO₄ or O₃) to (IV) and EtCO₂H; in the former case a little EtCHO is also produced]; the *aci*-forms of these nitro-olefines resemble that of (III). cycloPent-anone and MeNO₂ give a poor yield of chiefly 1-nitromethyl- Δ^1 -cyclopentene, b.p. 89—91°/14 mm., oxidised (KMnO₄) to glutaric acid. The above nitro-olefines exist solely in their $\beta\gamma$ -forms; this is attributed to the inductive effect of the NO₂-group, which increases the toleration of C₃ for covalent union with H. The mobility of such systems is not apparent. CORR' and MeNO₂ in presence of NaOEt, piperidine, C₂H₅N, NH₂Me, or "mol." Na give 15—25% of CRR'(CH₂NO₂)₂; $\alpha\gamma$ -dinitro- $\beta\beta$ -dimethyl-, b.p. about 135—138°/9 mm., m.p. 89—90°, - β -methyl- β -ethyl-, b.p. 135—138°/9 mm., - $\beta\beta$ -diethyl-, b.p. 135—138°/10 mm., and - β -methyl- β -propyl-, b.p. 144°/11 mm., -propanes are described.

The structures of Et α -nitro- β -methyl- Δ^1 - (VI) and - Δ^2 -butenoate (VII) (Bouveault and Wahl, A., 1901, i, 5) are confirmed. (VI) is oxidised (KMnO₄) to COMe₂ and H₂C₂O₄ (also formed with a little CH₂O on ozonolysis), whilst (VII) is oxidised (O₃) to CH₂O, AcOH, and H₂C₂O₄. The NH₄ derivative of NO₂-CH₂-CO₂Et (VIII) has m.p. 131° (cf. *loc. cit.*). (VI) and (VII) do not give colours with FeCl₃; aq. solutions do so after keeping and become faintly acid.

(VII) can be titrated rapidly with alkali in EtOH. Acidification of the K derivative from (VI) with dil. HCl gives (VII) containing no measurable amount of the *aci*-form; equilibrium between NO_2^- and *aci*-form is established very rapidly probably owing to the additional activation due to the CO_2Et group. Acidification with $\text{Et}_2\text{O}-\text{BzOH}$ affords a mixture of (VI) and (VII) showing that there is a definite tendency in these compounds for a redistribution of the anionic charge in the three-carbon system, also owing to the presence of the CO_2Et group. *Et* α -nitrocyclohexylideneacetate (IX), b.p. $130-134^\circ/4$ mm. [oxidised (KMnO_4 or O_3) to (I)], is prepared by nitration of *Et* cyclohexylideneacetate; it could not be obtained from (I) and (VIII). Successive treatment of (IX) with $\text{Et}_2\text{O}-\text{NH}_3$ and dil. acid gives (I) and (VIII), whilst cautious acidification of the K derivative (X) of (IX) affords *Et* α -nitro- Δ^1 -cyclohexenylacetate, b.p. $124-126^\circ/3$ mm. [oxidised (KMnO_4) to $\text{H}_2\text{C}_2\text{O}_4$ and (IV)], which could not be obtained by nitration of *Et* Δ^1 -cyclohexenylacetate. (X) does not react with *EtI* in C_6H_6 or Et_2O ; in *EtOH*, the *oxime*, m.p. 98° , of *Et* Δ^1 -cyclohexenylpyruvate is probably formed. *Et* α -nitro- β -ethyl- Δ^α -pentenoate, b.p. $119-122^\circ/13$ mm. [oxidised (KMnO_4) to COEt_2 and $\text{H}_2\text{C}_2\text{O}_4$], is prepared by nitration of $\text{CET}_2\text{:CH}\cdot\text{CO}_2\text{Et}$ and is converted through its K derivative into *Et* α -nitro- β -ethyl- Δ^β -pentenoate, b.p. $117-120^\circ/14$ mm. (ozonolysis products, MeCHO , AcOH , and EtCO_2H). *Et* α -nitro- β -methyl- Δ^α -hexenoate, b.p. $119-122^\circ/13$ mm. [oxidised (KMnO_4) to COMePr and $\text{H}_2\text{C}_2\text{O}_4$], is prepared from $\text{CMePr}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ and is similarly converted into *Et* α -nitro- β -methyl- Δ^β -hexenoate (?), b.p. $118-120^\circ/14$ mm. [oxidised (O_3) to MeCHO , $\text{H}_2\text{C}_2\text{O}_4$, and PrCO_2H]. H. B.

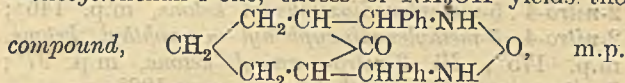
Reactions catalysed by aluminium chloride.

IX. Mechanism of ketone formation from cycloparaffins and acetyl chloride in presence of aluminium chloride. C. D. NENITZESCU and J. P. CANTUNARI (Annalen, 1934, 510, 269-279).—The formation of 2-acetyl-1-methyl-cyclopentane (I) and Δ^1 -cyclopentene (II) from cyclohexane (III), AcCl , and AlCl_3 involves the following reactions: (III) \rightarrow methylcyclopentane \rightarrow 1-methyl- Δ^1 -cyclopentene \rightarrow 1-chloro-2-acetyl-1-methylcyclopentane \rightarrow (I) (by loss of HCl and addition of 2H) or (II) (by loss of HCl) (this reaction occurs when the AlCl_3 is "poisoned"; cf. A., 1932, 1132). The results of Zelinski and Tarassova (*ibid.*, 1120; this vol., 295) are criticised; six-membered ring compounds are not formed in detectable amounts in the above reaction. Unger's work (A., 1932, 514) on the labile and stable forms of (I) is confirmed.

[With J. CHICOŞ and G. VÂNTU.] 1-Chloro-2-acetylcyclohexane, prepared by Wieland and Bettag's method (A., 1922, i, 1033) from cyclohexene, AcCl , and AlCl_3 , with an excess of AlCl_3 in (III) at room temp. gives cyclohexyl Me ketone, b.p. $180-181^\circ$ [also prepared by reduction (H_2 , Pd-C , MeOH) of 1-acetyl- Δ^1 -cyclohexene]; $\text{C}_6\text{H}_{10}\text{Cl}\cdot\text{COMe} + 2\text{H} \rightarrow \text{C}_6\text{H}_{11}\cdot\text{COMe} + \text{HCl}$ (the 2H are formed thus: $2\text{C}_6\text{H}_{12} \rightarrow \text{C}_{12}\text{H}_{22} + 2\text{H}$). cycloHexylmethylcarbinol [acetate, b.p. 208° (corr.)] has b.p. 190° (corr.), whilst 2-methylcyclopentylmethylcarbinol (acetate, b.p. 192°),

obtained by reduction (Na , aq. MeOH , Et_2O) of (I) or (II), has b.p. 177° . H. B.

Masking of certain chemical functions. R. POGGI and P. SALTINI (Gazzetta, 1934, 64, 189-191; cf. A., 1931, 1057; 1932, 1032).—With 2:6-dibenzylidene-cyclohexan-1-one, excess of NH_2OH yields the



$199-200^\circ$ (gas). As in the interaction of NH_2OH and pinacolin, the CO group appears to take no part in the reaction. T. H. P.

Action of sulphur on ketones. T. W. JEZERSKI (Rocz. Chem., 1934, 14, 216-221).— COPhMe (I) yields diphenacyl (II) on heating with S at $155-175^\circ$ for 7.5 hr. in an atm. of N_2 ; at $180-210^\circ$ thioindigo (III) is also obtained. (III) is not obtained from (II) and S at $180-210^\circ$, and must originate directly from (I). The sole products yielded by α - or β -naphthyl Me ketone are 1:2- and 2:1-naphthathioindigo. R. T.

Second-order Beckmann rearrangement. A. H. BLATT and R. P. BARNES (J. Amer. Chem. Soc., 1934, 56, 1148-1151).—*p*-Bromophenyl styryl ketoxime and PhSO_2Cl in $\text{C}_5\text{H}_5\text{N}$ at room temp. give the normal rearrangement product cinnam-*p*-bromoanilide. The oxime of benzoyldiphenylcarbinol (phenylbenzoin) (I) when similarly treated affords COPh_2 and PhCN , and the *oxime*, m.p. 125° , of α -benzoyl- α -phenylethyl alcohol (methylbenzoin) (II) gives COPhMe and PhCN ; these second-order rearrangements are considered to be essentially cleavage reactions. (I) is cleaved by aq. $\text{EtOH}-\text{KCN}$ to COPh_2 and PhCHO [which is then converted into benzoin (III)]; (II) similarly gives COPhMe and (III), which condense further to $\text{COPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{COPh}$; α -benzilmonoxime affords BzOH and PhCN ; β -benzilmonoxime yields PhCN ; α -benzoinoxime (?) furnishes PhCHO and PhCN , whilst β -benzoinoxime (IV) is completely destroyed. Mandelanilide [the normal rearrangement product of (IV)] and PCl_5 in Et_2O give $\text{CHClPh}\cdot\text{CO}\cdot\text{NHPh}$ and not PhNC (cf. Buck and Ide, A., 1931, 844), indicating that the second-order rearrangement (formation of PhNC) of (IV) is not normal rearrangement followed by cleavage. α -Benzoinoxime acetate (V) and cold aq. 5% NaOH give PhCHO , PhCN , and AcOH ; fission does not occur with β -benzoinoxime acetate (VI), since (IV) is produced. Thermal decomp. of (V) and (VI) gives PhCHO and PhCN ; α -benzilmonoxime acetate affords BzOH and PhCN , whilst the β -isomeride is unaffected at 190° . H. B.

Indones. Synthesis of 1-phenyl- α -naphthind-en-3-one. F. PIRONE (Atti R. Accad. Lincei, 1934, [vi], 19, 102-108).—The action of $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ on α - $\text{C}_{10}\text{H}_7\cdot\text{COPh}$ under de Fazi's conditions (A., 1919, i, 529) but for 8 hr. yields *Et* β -phenyl- β -1-naphthyl-lactate, m.p. $113-114^\circ$, which, on hydrolysis with conc. H_2SO_4 , gives first the corresponding two substituted cinnamic acids and then (1) 1-phenyl- α -naphthinden-3-one, m.p. $133-134^\circ$, and (2) 1-phenyl-perinaphthinden-3-one, m.p. $142-143^\circ$. T. H. P.

Preparation of aromatic nitro-ketones. S. BERLINGOZZI (Atti R. Accad. Lincei, 1934, [vi], 19,

332—336).—Treatment of an aromatic nitro-aldehyde with an aromatic magnesyl compound ($MgRCl$) gives the nitro-carbinol ($NO_2 \cdot C_6H_4 \cdot CHR \cdot OH$), which is oxidised to the nitro-ketone by CrO_3 . The following were thus prepared: *o*-, m.p. 122°, *m*-, m.p. 117°, and *p*-nitrophenyl α -naphthyl ketone, m.p. 95°; *Ph* 2-nitro-4:5-methylenedioxyphenyl ketone, m.p. 146°; 2-nitro-4:5-methylenedioxyphenyl α -naphthyl ketone, m.p. 175°; *Ph* 3-nitro-*p*-anisyl ketone, m.p. 97°; 3-nitro-*p*-anisyl α -naphthyl ketone, m.p. 102°.

T. H. P.

Reversibility of the Friedel-Crafts reaction. Interconversion of $\beta\beta$ -diphenylethyl *tert*-butyl ketones. H. H. WEINSTOCK, jun., and R. C. FUSON (J. Amer. Chem. Soc., 1934, 56, 1241—1242).—*p*-Chlorostyryl *Bu*^v ketone, m.p. 85—85.5° (from $COMeBu^v$ and *p*- $C_6H_4Cl \cdot CHO$ in aq. $EtOH-NaOH$), C_6H_6 , $AlCl_3$, and HCl (cf. A., 1933, 1170) give $\beta\beta$ -diphenylethyl *Bu*^v ketone (I), m.p. 83.5—84.5°, also obtained similarly from $CHPh \cdot CH \cdot COBu^v$ and *o*-chlorostyryl *Bu*^v ketone, m.p. 53.5—54.5°. With $PhCl$ instead of C_6H_6 , $\beta\beta$ -*di-p*-chlorophenylethyl *Bu*^v ketone (II), m.p. 153—153.5° [oxidised (alkaline $KMnO_4$) to 4:4-dichlorobenzophenone], results. (II) is similarly obtained from (I) and $PhCl$, whilst (II) and C_6H_6 give (I). Addition of aromatic compounds to the $C:C \cdot CO$ group is thus reversible.

H. B.

Phototropism of semicarbazones of ethylenic ketones. III. Thiosemicarbazones and δ -phenylsemicarbazones. C. V. GHEORGHIU (Bull. Soc. chim., 1934, [v], 1, 97—105; cf. this vol., 656).—Styryl Me ketone (I), α -piperonylidene- (II), α -piperonylidene- γ -methyl-, α -*p*-isopropylbenzylidene- (III), α -*o*-methoxybenzylidene- γ -methyl-, γ -*p*-hydroxybenzylidene-, γ -*o*-methoxybenzylidene-butan- β -one, α -*p*-isopropylbenzylidene- (IV), and γ -anisylidene-pentan- β -one (V) afford thiosemicarbazones (VI), m.p. 146—147°, 170—172°, 157°, 138°, 118—120°, 134—135°, 212—214°, 130—132°, and 168—169°, respectively, all of which are phototropic. (I), *o*-hydroxybenzylidenebutan- β -one (VII), (III), (IV), α -piperonylidene-pentan- β -one, (II), and (V) afford δ -phenylsemicarbazones (VIII), m.p. 186—189° (decomp.), 168°, 173—174°, 183—184°, 175°, 180—190°, and 158—161°, respectively, all of which [except (V)] are phototropic. (V) shows "inverse phototropism" in both compounds, and the (VIII) of (VII) is reversibly phototropic. Many ketones of the type $CHAr \cdot CH(or R) \cdot CO \cdot R$ ($R = alkyl$) fail to give (VI) or (VIII), probably due to the mutual influence of R and CO . The (VI) are also thermochromic, the (VIII) much less so.

J. L. D.

Structure of oximes and semicarbazones from their colour. (MME.) RAMART-LUCAS and (MME.) BRUZAU (Bull. Soc. chim., 1934, [v], 1, 119—141; cf. A., 1933, 1278).—The oximes of many deoxybenzoin (I), *meso*-methyl- (II) and *meso*-dimethyldeoxybenzoin (III) have similar absorption spectra, by measuring which it is deduced that the oximes of (I) contain the grouping $>C:N \cdot$ (A) or $>C:C \cdot NH \cdot$ (B), whereas those of (III) have the *iso*-structure $>C \begin{matrix} O \\ \diagdown \\ NH \end{matrix}$ (C).

Oximes of (II) consist of mixtures of (A) or (B), and (C). The following oximes are described: *p*-methyl-

m.p. 130—131°; *p*-methoxy-, m.p. 118—119°; *meso*-dimethyl-, m.p. 192—193°; *meso*-dimethyl-*p*-methyl-, m.p. 205—206°, and *meso*-dimethyl-*p*-methoxy-deoxybenzoin, m.p. 193—194°. The semicarbazones show parallel absorption properties. *meso*-Methyldeoxybenzoin affords two semicarbazones, m.p. 159° (mainly transparent form) and 212° (mainly absorbing form). The following semicarbazones are described: *p*-methoxy-, m.p. 148—149°; *meso*-methyl-*p*-methyl-, m.p. 150—151°; *meso*-methyl-*p*-methoxy-, m.p. 125—126°; *meso*-dimethyl-, m.p. 179°; *meso*-dimethyl-*p*-methyl-, m.p. 223—224°; *meso*-dimethyl-*p*-methoxy-deoxybenzoin, m.p. 210—211°; *p*-methoxybenzophenone, m.p. 179—180° and 151—152° (*syn*- and *anti*-forms); α -phenylethyl Me ketone, m.p. 172—173°, and α -methyl- α -phenylethyl Me ketone, m.p. 185—186° and 163—164° (*syn*- and *anti*-forms). J. L. D.

Grignard reaction in synthesis of ketones. V. Preparation of isomeric *p*-chlorobenzoinis. S. S. JENKINS (J. Amer. Chem. Soc., 1934, 56, 1137—1138).—*p*- $OMe \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot NH_2$ and *p*- $C_6H_4Cl \cdot MgBr$ (3 mols.) give *p*-chlorophenyl *p*-methoxybenzyl ketone, m.p. 111° (all m.p. are corr.) [oxime, m.p. 87.5—88°, converted by PCl_5 in Et_2O into *p*-methoxyphenylacet-*p*-chloroanilide, m.p. 138°, also prepared from *p*- $OMe \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$ and *p*- $C_6H_4Cl \cdot NH_2$ at 180—190°], brominated (method: this vol., 526) to *p*-chlorophenyl α -bromo-*p*-methoxybenzyl ketone (I), m.p. 85.5—86°. Anisyl α -bromo-*p*-chlorobenzyl ketone, m.p. 106.5°, and (I) are converted as described previously (*loc. cit.*) into anisoyl-*p*-chlorophenylcarbinol, m.p. 84.5—85.5°, and *p*-chlorobenzoyl-anisylcarbinol, m.p. 70.5—71.5°, respectively; these are both oxidised (Fehling's solution) to 4-chloro-4-methoxybenzil, m.p. 129.5°.

H. B.

Chlorides of dimethylanhydracetonebenzil. C. F. H. ALLEN and E. W. SPANAGEL (Canad. J. Res., 1934, 10, 315—317).—Dimethylanhydracetonebenzil and $AcCl$ give chiefly the chloride $\begin{matrix} CPh=CH \\ CPhCl \cdot CMe_2 > CO \end{matrix}$ (I) which is easily isomerised to $\begin{matrix} CPh \cdot CHCl \\ CPh \cdot CMe_2 > CO \end{matrix}$, m.p. 120° (cf. Burton *et al.*, A., 1933, 826). Hydrolysis of (I) may yield the OH-compound $\begin{matrix} CPh \cdot C(OH) \\ CHPh \cdot CMe_2 > CO \end{matrix}$ or sometimes the bimol. compound $\left[\begin{matrix} CPh-O \\ CPh \cdot CMe_2 > CO \end{matrix} \right]_2$, m.p. 181°.

F. R. S.

Anthrone series. V. Structure of so-called aglycone of aloin. T. F. McDONNELL [with J. H. GARDNER] (J. Amer. Chem. Soc., 1934, 56, 1246—1247).—Aloin (from Curacao aloes) and aq. borax give aloe-emodin-9-anthrone (I), m.p. 201—202.5° (all m.p. are corr.) (cf. Hauser, A., 1932, 370; Cahn and Simonsen, *ibid.*, 1252) (anthranyl acetate, m.p. 197.2—197.8°), reduced ($SnCl_2$, $AcOH$ -conc. HCl) to 1:8-dihydroxy-3-methyl-9-anthrone (*ibid.*, 164), which is oxidised (CrO_3 , $AcOH$) to chrysophanic acid. (I) is, therefore, 1:8-dihydroxy-3-hydroxymethyl-9-anthrone.

H. B.

Derivatives of hydroxyphloroglucinol. G. BARGELLINI and S. M. ZORAS (Gazzetta, 1934, 64, 192—202).—The action of $AcCl$ and $AlCl_3$ on 1:2:3:5-

$C_6H_2(OMe)_4$ in CS_2 yields: (1) 2:3:4:6-tetrahydroxyacetophenone Me_4 ether, m.p. 53—54° (not 43—45°; cf. A., 1911, i, 211; also Chapman *et al.*, A., 1928, 183); (2) the Me_3 ether, m.p. 112—113° (not 105—107°, *loc. cit.*); (3) the Me_2 ether (*loc. cit.*); (4) products, m.p. 160—180°, probably containing the compounds, m.p. 177—178° and 162—163°, of Chapman *et al.* (*loc. cit.*) and Hattori (A., 1931, 493; 1932, 64). When heated with Ac_2O and $NaOAc$, (2) gives 5:7:8-trimethoxy-4-methylcoumarin; Hattori's conclusion that (2) is 2-hydroxy-3:4:6-trimethoxyacetophenone is thus confirmed. Condensation of (2) with anisaldehyde gives 2'-hydroxy-3:4:6'-4-tetramethoxychalkone, m.p. 138—140°.

T. H. P.

Substantive dyes of the β -diketone type. W. LAMPE, J. MAJEWSKA-MEOSZEWSKA, T. CZYSTO-HORSKI, and T. SKULIMOWSKI (Rocz. Chem., 1934, 14, 222—232).— $CHNaAc \cdot CO_2Et$ (I) and piperonyl chloride at 100° yield *Et* α -piperonylacetate, m.p. 92—94°, which is converted into *Et* piperonylacetate (II), m.p. 73—75°, when kept at room temp. for 24 hr. with 10% aq. NH_3 . The *K* salt of (II) condenses with cinnamoyl chloride at room temp. to *Et* cinnamoylpiperonylacetate (III), m.p. 135—137°, and with *p*-carbomethoxycinnamoyl chloride to *Et* *p*-carbomethoxycinnamoylpiperonylacetate m.p. 176—177°. (III) is converted into cinnamoylpiperonylmethane (IV), m.p. 133—135°, by heating. β -Styrylacrylyl chloride (V) and (I) condense to yield *Et* α -(β -styrylacrylyl)acetoacetate (VI) (*Cu* salt, m.p. 193—196°), from which β -styrylacrylylacetone, m.p. 140—142°, is obtained by autoclaving with H_2O . Cinnamoyl- β -styrylacrylylmethane (VII), m.p. 153—155°, is prepared from (IV) and the *Na* salt of cinnamoylacetone. (VI) decomposes on keeping during 3 days with aq. NH_3 to yield *Et* β -styrylacrylylacetate (VIII), m.p. 81—83°, the *Na* salt of which condenses with (IV) to afford *Et* *di*- β -styrylacrylylacetate, m.p. 166—168°, and this, on autoclaving, yields *di*- β -styrylacrylylmethane (IX), m.p. 189—191°. (V) and $CHNaAc \cdot CO_2Me$ condense to the *Me* analogue (X), m.p. 58—60°, of (VI), and this gives similarly the *Me* analogue, m.p. 90—92°, of (VIII), into which it is converted by heating with $KOEt$ in $EtOH$. (X) yields *Me_2* α β -*di*-(β -styrylacryloyl)succinate, m.p. 182—184°, on adding I to its *Na* salt in Et_2O , and *Me* *p*-carbomethoxy-*m*-methoxycinnamoyl- β -styrylacrylylacetate (XI), m.p. 144—147°, on adding *p*-carbomethoxy-*m*-methoxycinnamoyl chloride to its *Na* salt. On autoclaving, (XI) affords *p*-carbomethoxy-*m*-methoxycinnamoyl- β -styrylacrylylmethane, m.p. 139—141°, and this, on keeping with 5% $NaOH$, yields *p*-hydroxy-*m*-methoxycinnamoyl- β -styrylacrylylmethane (XII), m.p. 156—159°. (IV), (VII), (IX), and (XII) are substantive yellow dyes for cotton.

R. T.

Constitution of carthamin. G. BARGELLINI and S. M. ZORAS (Gazzetta, 1934, 64, 202—212).—The different m.p. for 4:2':3':4':6'-pentamethoxychalkone given by Bargellini and Bini (A., 1911, i, 212) (88—90°) and Kuroda (J.C.S., 1930, 752, 765) (112°) are due to the existence of a metastable form, m.p. 95—96° (trigonal; $a:b:c=0.5708:1:0.7506$; α 73° 46', β 102° 9', γ 72° 12'),

which passes into the stable form, m.p. 111—112° (monoclinic; $a:b:c=1.1267:1:0.83412$; β 58° 10' 5''), when heated. Similarly 3:4:2':3':4':6'-hexamethoxychalkone (cf. Bargellini, A., 1919, i, 545) exists in metastable (m.p. 114—116°) and stable (m.p. 127—128°) forms. Condensation of 2-hydroxy-3:4:6-trimethoxyacetophenone with anisaldehyde gives 2'-hydroxy-3':4':6':4-tetramethoxychalkone, m.p. 138—140° (*Ac* derivative, m.p. 146—147°), and this, when heated with HCl or H_2SO_4 in $EtOH$, yields 5:7:8:4'-tetramethoxyflavanone, m.p. 138—140°, which, on the basis of Kuroda's constitution of carthamin, is carthamin Me_4 ether. T. H. P.

Flavanone series. P. C. MITTER and S. K. SAHA (J. Indian Chem. Soc., 1934, 11, 257—264).—Interaction of 2:4-dimethoxybenzaldehyde with $CH_2(CO_2H)_2$ in boiling C_5H_5N containing piperidine during 1 hr. affords 2:4-dimethoxycinnamic acid (I), m.p. 187°, which cannot be demethylated. β -Resorcylaldehyde with $ClCO_2Me$ in $COMe_2-NaOH$ affords dicarbomethoxybenzaldehyde (II), m.p. 72° (phenylhydrazone, m.p. 138°; semicarbazone, m.p. 185°), oxidised ($KMnO_4$ at 40—45°) to dicarbomethoxybenzoic acid, m.p. 159°. (II) with $CH_2(CO_2H)_2$ in $AcOH$ at 100° during 16 hr. affords some dicarbomethoxycinnamic acid, m.p. 190°, and carbomethoxyumbelliferonecarboxylic acid, m.p. 201—202°, which when boiled with 10% Na_2CO_3 during 15 min. affords umbelliferonecarboxylic acid, m.p. 262°, decarboxylated just above its m.p. Phloracetophenone Me_3 ether (A., 1899, i, 891) and dimethyl- β -resorcylaldehyde (III) in warm $EtOH$ containing 5% $NaOH$ afford 2:4:6:2':4'-pentamethoxychalkone (IV), m.p. 124°, which is different from the methylated product of fission of cyanomaclurin (J.C.S., 1905, 87, 715) with alkali. (IV) is reduced (H_2-Pt) in $EtOAc$ during 3 hr. to 2:4:6:2':4'-pentamethoxydihydrochalkone (V), m.p. 80° (oxime, m.p. 142°; semicarbazone, m.p. 134°), which condenses with piperonal in $EtOH$ containing $NaOH$ to 2:4:6-trimethoxybenzoyl-2':4'-dimethoxybenzyl-3'':4'':methylenedioxybenzylidenemethane, m.p. 215°. Phloracetophenone Me_2 ether with (III) in $EtOH-NaOH$ affords 2-hydroxy-4:6:2':4'-tetramethoxychalkone, m.p. 125° (lit. 152°), converted with difficulty into an impure flavanone, and reduced (H_2-Pt) in $EtOAc$ to 2-hydroxy-4:6:2':4'-tetramethoxydihydrochalkone, m.p. 100°, methylated to (V). J. L. D.

Bisdi-indonylenes. cis-Bisdi-indonylene. G. WANAG (Annalen, 1934, 510, 280—287; cf. A., 1932, 746).—Successive treatment of *trans*- α' -diphthaloyl- β -*di*-*o*-carboxyphenyl- Δ^{ac} -hexatriene (I) (*loc. cit.*) with $Br-H_2O$ and aq. $NaHSO_3$ gives a mixture of *cis*-bisdi-indonylene (II), green, m.p. 344° (decomp.) (*Cu* block), and *trans*-dioxidobisdi-indonylene (III); (II) probably arises by loss of Br from bisdi-indonylene dibromide, which is formed by loss of $2H_2O$ from the dibromide of (I). Solutions of (II) in $CHCl_3$ are stable, but in many solvents (*e.g.*, hot $CH_2Ph \cdot OAc$) rapid isomerisation to the *trans*-form (IV) (*loc. cit.*) occurs. Hydrolysis (dil. $NaOH$) of (II) gives (I), whilst autoxidation (Br in $CHCl_3$ followed by evaporation in air) affords (III). (II) and Br in $AcOH$ at 100° (bath) give dibromodi-indone (V),

$C_6H_4 \begin{matrix} \diagup CO \\ \diagdown CO \end{matrix} C:C \begin{matrix} \diagup C_6H_4 \\ \diagdown CBr_2 \end{matrix} CO$, m.p. 251°, fission of a C:C linking taking place. Oxidation (PbO₂, CHCl₃) of bromodi-indone affords (II) and (V) [probably formed owing to the liberation of Br from the first formed dibromide of (II)]. Di-indone (VI) and (V) with K₂CO₃ in C₆H₆ give (II) and a little (IV), whilst (V) and (VI) in C₅H₅N afford a little (IV) and a compound, probably $C_6H_4 \begin{matrix} \diagup CO \\ \diagdown CO \end{matrix} C:C \begin{matrix} \diagup C_6H_4 \\ \diagdown CH \end{matrix} C-C_5H_4N$, m.p. 290°. H. B.

Instance of the reversed field effect of the methyl group. J. KENNER and F. MORTON (J.C.S., 1934, 679—680).—The failure (A., 1931, 1061) to obtain a quinone by thermal decomp. of 4-nitro-2:6-di-*o*-tolylphenol is ascribed to the reversed field effect of the Me groups (Bennett and Mosses, A., 1930, 1555; cf. A., 1933, 499). In agreement with this view, 4-nitro-2:6-di-*o*-chlorophenylphenol (I), m.p. 140° (Me ether, m.p. 107°), furnishes a coloured Na salt and decomposes in boiling AcOH to 2:6-di-*o*-chlorophenyl-*p*-benzoquinone (II), m.p. 103°, best prepared by oxidation [Pb(OAc)₄, AcOH] of (I). 4-Amino-2:6-di-*o*-chlorophenylphenol hydrochloride, m.p. 231°, is oxidised (aq. CrO₃) to (II). *m*-Chlorophenylacetonitrile, b.p. 261°/757 mm., m.p. 11.5° (from the chloride), is hydrolysed (H₂SO₄, AcOH, H₂O) to *m*-chlorophenylacetic acid, m.p. 76° (cf. Muenzen *et al.*, A., 1926, 972). Distillation of the Pb salts of C₆H₄Cl·CH₂·CO₂H gives 2:2', m.p. 102° (oxime, m.p. 112°; semicarbazone, m.p. 149°), 3:3', m.p. 89° (oxime, m.p. 73°; semicarbazone, m.p. 121°), and 4:4'-dichlorodibenzyl ketone, m.p. 93° (oxime, m.p. 135—136°; semicarbazone, m.p. 118°); with nitromalonaldehyde, these afford (I), 4-nitro-2:6-di-*m*-, m.p. 177—178° (Me ether, m.p. 131°), and -*p*-chlorophenylphenol, m.p. 202° (Me ether, m.p. 190°), respectively. 2:6-Di-*m*-, m.p. 183°, and -*p*-chlorophenyl-*p*-benzoquinone, m.p. 263°, are prepared [as (II)]. 4-Amino-2:6-di-*m*- and -*p*-chlorophenylphenol hydrochlorides have m.p. 254° and 247°, respectively.

H. B.

Chemistry of lipins of tubercle bacilli. XXXVIII. New synthesis of phthiocol, the pigment of the human tubercle bacillus. M. S. NEWMAN, J. A. CROWDER, and R. J. ANDERSON (J. Biol. Chem., 1934, 105, 279—281; cf. this vol., 192).—Phthiocol (3-hydroxy-2-methyl-1:4-naphthaquinone) is formed in 41% yield when 3-hydroxy-1:4-naphthaquinone-2-acetic acid is decarboxylated by heating with Cu Ba chromite catalyst (A., 1932, 477). A. E. O.

Molecular compounds of halogenated anthraquinones with metallic salts. K. BRASS and H. EICHLER (Ber., 1934, 67, [B], 779—787; cf. A., 1931, 1061).—The mol. compounds of halogenoanthraquinones and SbCl₅ prepared in CHCl₃ are washed with CHCl₃ and preserved in a vac. (method A) or washed with light petroleum and not placed in a vac. (method B). The mol. ratio of the adducts varies greatly, and is not conditioned by the nature and position of the halogen. The commonest ratio is 1:2. The introduction of halogen at 1 or 2 in anthraquinone does not appear to alter the available

valency, although occasionally an increase is observed. The following compounds of anthraquinone derivatives with SbCl₅ are described, the method of prep. and the mol. ratio being placed in parentheses; the addition of a third no. indicates mols. of CHCl₃: 2-chloro- (A, 1:2; B, 1:2:1; A, 1:2:2; A, 1:3; A, 1:4); 1-bromo- (A, 1:1:2; A, 1:2; A, 1:2:1; B, 1:3:8); 2-bromo- (A or B, 1:2; A or B, 1:2:1; B, 1:3:8; B, 2:1:16); 1-iodo- (A, 1:2); 2-iodo- (B, 1:2; B, 2:4:1; B, 1:2:1; A, 1:3:6; A, 1:4:4; B, 2:5:1); 1:5-dibromo- (B, 1:1). 1:8-Dibromo- and 1:3-dichloro-anthraquinone do not combine with SbCl₅. Quinizarin gives mol. compounds, 2:1:1 and 1:1:1. 6:7-Dichloroquinizarin yields the substances 4C₁₄H₆O₄Cl₂·SnCl₃, 2C₁₄H₆O₄Cl₂·SbCl₄·CHCl₃, and 4C₁₄H₆O₄Cl₂·7SbCl₄. H. W.

Quinones. I. Preparation of anthraquinone and phenanthraquinone by hydrolysis of their monoximes. C. L. TSENG, M. HU, and E. J. H. CHU (J. Chinese Chem. Soc., 1934, 11, 47—56).—Anthraquinonemonoxime (cf. A., 1902, i, 795) with boiling dil. HCl during 0.5 hr. readily affords anthraquinone (95%). Phenanthraquinonemonoxime with boiling HCl and CH₂O during 3—5 hr. affords the quinone (92%). J. L. D.

Biochemistry of micro-organisms. XXXVII. Production of hydroxyanthraquinones by species of Helminthosporium. Isolation of tritisporin. Constitution of catenarin.—See this vol., 697.

Resinols. II. Oxidation of α- and β-amyrins with chromic anhydride. F. S. SPRING and T. VICKERSTAFF (J.C.S., 1934, 650—651).—Oxidation (CrO₃) of β-amyrin gives β-amyrone oxide, m.p. 237°, [α]_D²⁰ +143° in CHCl₃ (semicarbazone, m.p. 232°), and two oxide-dicarboxylic acids C₃₀H₄₈O₅, m.p. 252° and m.p. 286° (Me₂ ester, m.p. 268°, [α]_D²⁰ +137° in CHCl₃). α-Amyrin and α-amyrone similarly afford α-amyrone oxide, m.p. 193°, [α]_D²⁰ +141° in CHCl₃ (semicarbazone, m.p. 223°), and an acid, C₃₀H₄₈O₅ (Me₂ ester, m.p. 251°, [α]_D²⁰ +170° in CHCl₃). The cyclic group ·CH₂·CH(OH)CH₂· is indicated in β-amyrin.

F. R. S.

Resins. III. Action of ozone on α- and β-amyrin. P. HORMANN and J. MAERINIUS (Arch. Pharm., 1934, 272, 607—642; cf. A., 1930, 215).—Unless otherwise stated the following results refer to both α- (I) and β-amyrin (II). The O taken up by amyrin with 8% O₃ in EtOAc increases with time of ozonolysis to a max. of 32% (110) and in CCl₄ to 20%. The amount of acid products formed on decomp. increases with the degree of ozonolysis. The ozonide obtained in CCl₄ retains much CCl₄, which accounts for the high O contents previously recorded. The product (22.5% O) obtained in EtOAc, when decomposed with N-KOH or H₂O, gives COMe₂, a ketone (IV), C₂₁H₃₄O, m.p. 155—156°, [α]_D²⁰ +141.2° in CHCl₃ [from (I); ketone from (II) has α 0°] [semicarbazone, m.p. 290—291° (decomp.); oxime, m.p. 217—218° (decomp.)], an acid, OH·C₁₈H₂₈·CO₂H, amorphous, m.p. about 140—152° (decomp.) (Ag salt), and indefinite substances. The ozonide obtained in CCl₄ from (I) with H₂O gives COMe₂, (IV), an unsaturated substance, C₂₁H₃₃O₂·OH, m.p. 95°, [α]_D²⁰

+89.7° in CHCl_3 , and an acid, $\text{C}_{21}\text{H}_{33}(\text{OH})_2\cdot\text{CO}_2\text{H}$, amorphous, m.p. 112—160° (decomp.) (Ag salt).

R. S. C.

Lonchocarpic acid, a new compound from a species of *Lonchocarpus*. H. A. JONES (J. Amer. Chem. Soc., 1934, 56, 1247—1248).—Addition of CCl_4 to the conc. COMe_2 extract of the bark and inner portion of the root of an unknown species of *Lonchocarpus* gives 3.7 and 1.5%, respectively, of *lonchocarpic acid*, $\text{C}_{26}\text{H}_{26}\text{O}_6$, m.p. 201.5° (occasionally 220—221°), which contains 1 OMe.

H. B.

Toad poisons. V. Bufagin and bufalin. M. KOTAKE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 39—48; cf. A., 1928, 1138).—Bufagin (prep. described) with Ac_2O containing NaOAc at 100° during 5 hr. affords diacetylbufagin (I) and anhydroacetylbufagin (II), $\text{C}_{26}\text{H}_{36}\text{O}_5$, which with conc. HCl at room temp. during several hr. gives a product, m.p. 267—268° (Ac derivative, m.p. 234°). (II) affords with MeOH -50% KOH at room temp. during several hr. *anhydrobufalinic acid*, $\text{C}_{24}\text{H}_{36}\text{O}_5$, m.p. 211—212°. (I) in boiling MeOH - NH_3 during 3.5 hr. affords a product, $\text{C}_{30}\text{H}_{40}\text{O}_8$, m.p. 224—228°, different from (II).

J. L. D.

Guaiazulene. K. S. BIRRELL (J. Amer. Chem. Soc., 1934, 56, 1248).—The S- and Se-guaiazulenes of Ruzicka and Haagen-Smit (A., 1931, 1301) are probably identical; they are obtained solid (both m.p. 31.5°) by cooling in liquid air.

H. B.

Effect of selenious acid on terpenes. Synthesis of carvotanacetone and Δ^3 -menthen-5-one. E. BORGWARDT and E. SCHWENK (J. Amer. Chem. Soc., 1934, 56, 1185—1187; cf. A., 1932, 1253).— Δ^1 -Menthene and SeO_2 in EtOH give carvotanacetone (Δ^1 -menthen-6-one), b.p. 95°/7—8 mm. (semicarbazone, m.p. 177—178°), and some 1:2-*oxidomenthene*, b.p. 63—65°/0.25 mm., which is rearranged by boiling dil. H_2SO_4 to a ketone (semicarbazone, m.p. 140—142°). Δ^3 -Menthene similarly affords Δ^3 -menthen-5-one, b.p. 107—108°/12.5 mm. (semicarbazone, m.p. 176—177°), which when reduced (Na, EtOH) and then oxidised (CrO_3) gives 3-menthone. α -Phellandrene and piperitone are similarly oxidised and dehydrogenated to cumaldehyde and thymol, respectively.

H. B.

Resolution of *dl*-menthyl (–)mandelate. A. MCKENZIE and E. M. LUIS (J.C.S., 1934, 715—716).—Esterification (HCl) of (–)mandelic acid with *dl*-menthol and fractional crystallisation from EtOH and dil. AcOH gives (+)menthyl (–)mandelate (I), m.p. 98—99°, $[\alpha]_{\text{D}}^{20} +9.1^\circ$ in EtOH , also obtained by esterification with (+)menthol (II), and giving (II) on hydrolysis. Evaporation of a COMe_2 solution of (I) and (–)menthyl (–)mandelate gives *dl*-menthyl (–)mandelate, m.p. 76—77°, $[\alpha]_{\text{D}}^{20} -64.4^\circ$ in EtOH , which undergoes partial resolution on crystallisation from ligroin, (I) predominating in the crystals. Evaporation of an EtOH solution of (I) and (–)menthyl (+)mandelate affords *r*-menthyl *r*-mandelate, m.p. 80—81°.

J. W. B.

Acid products of oxidation of pinene. K. SŁAWINSKI and W. ZACHAREWICZ (Rocz. Chem., 1934, 14, 213—215).—67% of the acids produced by

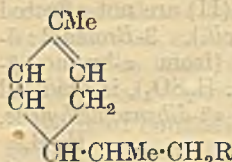
KMnO_4 oxidation of *l*-pinene consist of pinonic acid, and the remainder of α -pinonic acid.

R. T.

Optically inactive bornyl fumarates. A. MCKENZIE and E. B. ABBOT (J.C.S., 1934, 711—715).—Admixture of (–) and (+)bornyl fumarate in CHCl_3 affords *r*-bornyl fumarate (I) ($:\text{CH}\cdot\text{CO}_2\text{C}_{10}\text{H}_{17}\text{-r}$), m.p. 116—117°. (–)Bornyl (+)bornyl fumarate (II) [(+) $\text{C}_{10}\text{H}_{17}\text{O}_2\text{C}\cdot\text{CH}\cdot\text{CO}_2\text{C}_{10}\text{H}_{17}\text{-}$], m.p. 131°, is obtained (a) by heating (+)bornyl H fumarate (III) with (–)borneol at 130—140° (50% yield), (b) by heating (–)bornyl H fumarate (IV) with (+)borneol (V) (prep. of optically pure specimen described) (32% yield), some (I) and (+)bornyl fumarate also being formed, and (c) from (–)bornyl fumaryl chloride, b.p. 136—137°/4 mm., $[\alpha]_{\text{D}}^{20} -40.8^\circ$ in CHCl_3 [from (IV) and SOCl_2] and (V) in C_6H_6 . *r*-Bornyl H fumarate (VI), m.p. 118—119°, and dimorphous form, m.p. 125—126° (stable), is obtained by admixture of (III) and (IV) in CHCl_3 . Esterification of *dl*-borneol with fumaric acid gives (VI) and a mixture of (I) and (II), and half hydrolysis of (II) gives (VI).

J. W. B.

Volatile plant materials. II. Turmerone, the perfume of curcuma oil. H. RUPE, G. CLAR, A. S. PFAU, and P. PLATTNER (Helv. Chim. Acta, 1934, 17, 372—389).—The neutral portion (I), b.p. 155—156°/10 mm., of curcuma (turmeric) oil contains no OH (AcCl , Zerevitinov, CH_2N_2 , and PhNCO), but is mainly a mixture of ketones, and reacts with MgEtBr to give a hydrocarbon $\text{C}_{17}\text{H}_{26}$, b.p. 142°/10 mm., gives an amorphous semicarbazone, and only an (?) additive compound $\text{C}_{15}\text{H}_{23}\text{O}_2\text{N}$, m.p. 111° [from (II)] with NH_2OH . Fractional distillation of (I) affords pure *ar*-turmerone (II), b.p. 164°/10 mm., $[\alpha]_{\text{D}} +80.52^\circ$, which is *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}_2$, since O_3 gives COMe_2 and curcumatic acid (A., 1924, i, 1066), and with KOH - MeOH , COMe_2 , and curcumone (III) are obtained. With H_2 -Ni (II) affords a H_2 -derivative (IV), isolated as its oxime, b.p. 146.5—147°/1 mm. The following results show the presence of a sesquiterpene ketone turmerone $\text{C}_{15}\text{H}_{22}\text{O}$ (V), not isolated pure. Reduction of (I) with Ni-H_2 in 70% EtOH at room temp. gives a mixture, b.p. 142.5°/10 mm., of (IV) and hexahydro-turmerone, and Na-EtOH affords a mixture, b.p. 106—108°/1 mm., of dihydro-turmerol and dihydro-*ar*-turmerol (VI), which with Ni-H_2 in EtOH at 70°, gives a mixture, b.p. 108—110°/1 mm., of hexahydro-turmerol and (VI). Hydrolysis of (I) with KOH -aq. EtOH gives COMe_2 , 4-methyl- Δ^3 -cyclohexenyl Me ketone (identical with a specimen obtained from atlantone, which is thus present in traces), (III), and an unsaturated ketone which must be (A) ($\text{R}=\text{Ac}$), or its $\Delta^1:3$ - or $\Delta^1:4$ -isomeride (from (V)), dehydrogenated by FeCl_3 - AcOH in CO_2 to (III), and removed from the mixture by KMnO_4 oxidation or by addition of $(:\text{CH}\cdot\text{CO})_2\text{O}$. Determinations of the no. of double linkings in all these mixtures give expected vals. intermediate between those of (II) and (V); (V) is therefore (A) ($\text{R}=\text{CO}\cdot\text{CH}\cdot\text{CMe}_2$), or its $\Delta^1:3$ - or $\Delta^1:4$ -isomeride. From



(A.)

these results (I) contains 50% of (V), 40% of (II) [increasing on keeping, possibly due to auto-oxidation of (V)], and 10% of a sesquiterpene alcohol.

J. W. B.

Stability of the tetrahydrofuran ring. II. Dehydration of tetrahydrofurfuryl alcohol. R. PAUL (Bull. Soc. chim., 1933, [iv], 53, 1489—1495; cf. A., 1933, 954).—Tetrahydrofurfuryl alcohol and Al_2O_3 at 370—380° give Δ^2 -dihydropyran, b.p. 86—87° (44% yield), the dibromide, b.p. 106°/17 mm., 223—224° (corr.)/758 mm., of which with NH_2Ph gives *N*-phenylpiperidine [*picrate*, m.p. 144—146° (block)]; *platinichloride*, +2H₂O, decomp. 186—190°].

R. S. C.

Relative aromaticities. IV. Alkali furyls. H. GILMAN and F. BRÉUER (J. Amer. Chem. Soc., 1934, 56, 1123—1127).— NaR (R=Et, Ph, $-CH_2Ph$) (usually prepared *in situ* from HgR_2 and Na) and an excess of furan (I) give Na 2-furyl (II); removal of excess of (I) by distillation, addition of *n*-hexane, destruction of excess of Na by Hg, and treatment with CO₂ affords 2-furoic acid (5—58%) (III). 2-Methylfuran (IV) similarly gives a little 5-methyl-2-furoic acid (V), which may be formed as the result of an allylic rearrangement. 2-Methylthiophen and Na 2-thienyl in *n*-heptane similarly afford 21% of 5-methyl-2-thienoic acid. Na 2-thienyl (VI) (from Hg di-2-thienyl and Na) and (I) give (II); thiophen and (II) similarly afford (VI). K 2-furyl is obtained from (I) and liquid Na-K alloy; subsequent carbonation gives a little (III) and (mainly) an unidentified oil. (IV) similarly affords a little (V). (I) and $NaCPh_2$ give (II) (which reacts to a certain extent with $CHPh_3$), indicating that (I) is more acidic than $CHPh_3$. (I) is a weaker acid than $CH:CPh$. (II), prepared from Hg di-2-furyl and Na, is insol. and relatively stable in Et₂O. The above results also show that (I) is much more aromatic than C₆H₆ (cf. this vol., 415).

H. B.

Evidence for the $\alpha\delta$ -addition of hydrogen halides to $\alpha\beta$ -unsaturated ketones. Monohalogenodibenzoyl ethylenes. R. E. LUTZ and F. N. WILDER (J. Amer. Chem. Soc., 1934, 56, 1193—1195).—*cis*- α -Chloro- $\alpha\beta$ -dibenzoyl ethylene (I), m.p. 70.5—71° (all m.p. are corr.) [obtained from 3-chloro-2 : 5-diphenylfuran and HNO₃-AcOH or by the action of sunlight on the *trans*-isomeride (II) (designated the β -form in A., 1925, i, 681) in EtOH], and (II) with EtOH-HCl give the same mixture of (mainly) *meso*- $\alpha\beta$ -dichloro- $\alpha\beta$ -dibenzoyl ethane and 3 : 4-dichloro-2 : 5-diphenylfuran; the formation of the latter and the const. ratio of the products are explained only by the $\alpha\delta$ -addition of HCl. (I) and (II) are not affected by sunlight in $CHCl_3-I$ (cf. *loc. cit.*). 3-Bromo-2 : 5-diphenylfuran, m.p. 82—82.5° (from α -bromo- $\alpha\beta$ -dibenzoyl ethane, Ac₂O, and conc. H₂SO₄), is oxidised (HNO₃-AcOH) to *cis*- α -bromo- $\alpha\beta$ -dibenzoyl ethylene, m.p. 66.5°.

H. B.

Organic peroxides. III. Peroxides in furan series. IV. Spontaneous decomposition of furoyl hydrogen peroxide. N. A. MILAS and A. McALEVY (J. Amer. Chem. Soc., 1934, 56, 1219—1221, 1221—1225).—III. Furoyl chloride and Na₂O₂ in H₂O at $\pm 3^\circ$ give *difuroyl peroxide* (I),

m.p. 86—87° (decomp.), which explodes violently when heated or rubbed. β -Furylacrylyl chloride similarly affords (at $\pm 0^\circ$) *di*- β -furylacrylyl peroxide, m.p. 104° (decomp.), which also explodes violently when heated. (I) and MeOH-NaOMe in cold Et₂O give *furoyl hydrogen peroxide* (II), m.p. 59.5° (decomp.), which hydrolyses in aq. solution to furoic acid (III) and H₂O₂, but is stable in $CHCl_3$ at 0°. These peroxides are more unstable and more reactive than the corresponding compounds of the C₆H₆ and camphoric acid series (A., 1933, 279). The no. of mols. of (II) consumed when the following are treated in $CHCl_3$ at room temp. for 1 hr. are: *isoeugenol* 1.037, *isosafole* 1.081, *safrole* 1.015, *cholesterol* 1.02, *ergosterol* 3.127, *citronellol* 1.043, *pinene* 1.083, *limonene* 1.685, *geraniol* 1.38, $CMe_2:CMe_2$ 0.29, *allyl alcohol* 0.15, (III) 0. Irradiation of *furfuraldehyde* (IV) containing a little (II) in N₂ at 25° for 1 hr. does not cause complete disappearance of (II). (IV) absorbs O₂ when irradiated in air, but peroxide could not be detected; in light petroleum at 0°, (II) may be produced.

IV. Spontaneous decomp. of (II) (solid) at 0° occurs slowly after an induction period of 72 hr.; decomp. begins at "active spots" or "nuclei" (probably formed on the corners or edges of crystals). The induction period is shortened by raising the temp.; at 40°, detonation occurs. The effects of addition of various solids (org. and inorg.) are studied. Decomp. of (II), alone or in AcOH, is accelerated by light of 4500—3600 Å. Decomp. of (II) at 35° in a vac. gives (III) (50.7%), CO₂ (10.1%), an alkali-sol. polymeride (37%), and (probably) 4 : 5-epoxyfuroic acid (1.5%) (*Ba* salt). Decomp. of (II) in $CHCl_3$ at 35° and 40° is unimol. and (III) and O₂ are produced; the temp. coeff. is 2.3 and the heat of activation is 15,800 g.-cal. per mol.

H. B.

Geometrical isomerism of $\alpha\alpha'$ -disubstituted tetrahydro- γ -pyrones. R. CORNUBERT and P. ROBINET (Bull. Soc. chim., 1934, [v], 1, 90—97).—Interaction of acetonedicarboxylic acid with PhCHO (3 parts) and dry HCl at about 0° affords two stereoisomeric forms of $\alpha\alpha'$ -diphenyltetrahydropyrone, m.p. 131° [oxime (I), m.p. 154—155°] and 76° [oxime, m.p. 144—145°, different from (I)].

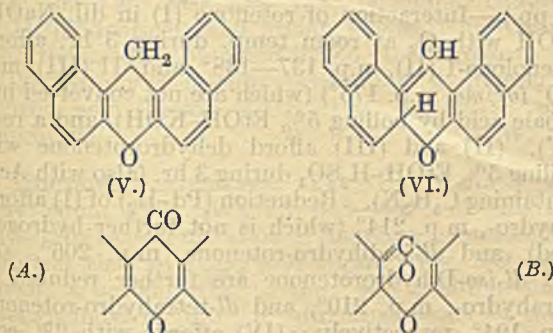
J. L. D.

Catalytic reduction of dehydracetic acid. R. MAŁACHOWSKI and T. WANCZURA (Bull. Acad. Polonaise, 1933, A, 547—557).—Reduction of dehydracetic acid with H₂-PtO₂ in MeOH affords 2-keto-6-methyl-3-ethyl-2 : 3-dihydro- γ -pyrone (I), m.p. 185° (oxime, m.p. 226°), hydrolysed by H₂O at 130° to *n*-heptane- $\beta\delta$ -dione. The *K* derivative of $CO \left\langle \begin{array}{l} CH:CMc \\ CH_2-CO \end{array} \right\rangle O$ with Et₂SO₄ at 105° gives, not (I), but the isomeric 4-ethoxy-6-methyl- α -pyrone, b.p. 142—148°/10 mm., m.p. 62°.

J. W. B.

s- $\alpha\beta$ -Dinaphtho- γ -pyrone. K. DZIEWOŃSKI, S. PIZOŃ, and (MLLE.) M. MAZURKIEWICZÓWNA. Two isomeric $\alpha\beta$ -dinaphthopyrans. K. DZIEWOŃSKI and S. PIZOŃ (Bull. Acad. Polonaise, 1933, A, 560—565, 566—572).—Oxidation of *dinaphtho- γ -methylpyrone* (I) (9-methyl-1 : 2 : 7 : 8-dibenzoxanthan) (from β -C₁₀H₇-OH and MeCHO; Claisen, A., 1887, 270, 494) with CrO₃ in AcOH affords 1 : 2 : 7 : 8-

dibenzoxanthone (II), the supposed 2:3:7:8-dibenzoxanthone, m.p. 149°, similarly obtained by Claus *et al.* (A., 1890, 510), being a mixture of (II) and unchanged (I). The anil (III) (A., 1932, 859) of (II) with H_2S in AcOH gives 1:2:7:8-dibenzo-thioxanthone, m.p. 210°. Condensation of β - $C_{10}H_7\cdot OH$ with the appropriate $CS(NHAr)_2$ affords the o-, m.p. 195—196.5° [4':6'-(NO_2)₂-derivative, m.p. 256—257°], and p-, m.p. 206—207°, -methyl- and p-chloro-, m.p. 193—195°, -anil of (II). With HI (*d* 1.96) and red P at 180° (II) or (III) affords 1- $C_{10}H_7$ Me. Distillation of di-(2-hydroxy-1-naphthyl) ketone with Zn dust, or treatment of 1:1':2:2'-dinaphthopyrylium bromide $[C_{10}H_6\langle\begin{smallmatrix} CH \\ O \end{smallmatrix}\rangle C_{10}H_6] Br'$ (IV) (Fosse, A., 1901, i, 604) with hot EtOH affords 1:2:7:8-dibenzoxanthen (V), m.p. 202° (Wolf, A., 1893, i, 222). Reduction of (II) or (III) with red P and HI at 150—160° gives the iso-form (VI), m.p. 185° (picrate, m.p. 197°). With Br in AcOH either (V) or (VI) gives



(IV). (V) and (VI) are regarded as derived, respectively, from the tautomeric forms (A) and (B) of (II).

J. W. B.

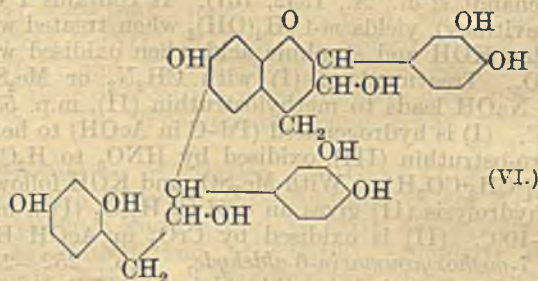
Diphenylene oxide series. IV. N. M. CULLINANE, H. G. DAVEY, and H. J. H. PADFIELD (J.C.S., 1934, 716—719).—Diphenylene oxide (best prepared in 20% yield by destructive distillation of PhOH with PbO) is also obtained (a) by heating pyrocatechol (I) and PhOH at 240°, some diphenylene dioxide (II) [prep. by condensation of (I) with o - $C_6H_4Cl_2$] also being formed if P_2O_5 is used, (b) by boiling the 2:2'-dihydroxydiphenyl [by diazotisation of the 2:2'-(NH_2)₂-compound] with H_2O , or (c) by heating 4:4'-dihydroxydiphenyl with P_2O_5 . By heating guaiacol, KOH, and o - $C_6H_4Cl\cdot NO_2$ at 190—195° is obtained 2-nitro-2'-methoxydiphenyl ether, m.p. 71°, converted by boiling HI (*d* 1.7) into the 2-amino-2'-hydroxy-compound, m.p. 116°, which by diazotisation and successive treatment with $CuSO_4$ and 50% H_2SO_4 gives (II), and at 270—280° affords phenoxazine. 2:2'-Dinitrodiphenyl ether (in 6% yield by heating o - $NO_2\cdot C_6H_4\cdot ONa$ with o - $C_6H_4Cl\cdot NO_2$ at 220°) is reduced by aq. EtOH- NH_3 - H_2S to the 2-nitro-2'-amino-derivative, m.p. 56°. With Br-AcOH 2-nitrodiphenylene oxide gives its 6-Br-derivative, m.p. 248°, also obtained from 3-bromo-diphenylene oxide (III) and HNO_3 (*d* 1.5)-AcOH. With Br-AcOH (III) affords the 3:6-Br₂-derivative.

J. W. B.

Composition of *Daphne genkwa*.—See this vol., 820.

Preparation of diphenylphenolphthalein [2-hydroxydiphenylphthalein] and substitution products.—See B., 1934, 556.

Tannins and similar substances. XXVII. Quebracho-tannin. K. FREUDENBERG and P. MAITLAND (Annalen, 1934, 510, 193—205).—Reduction (H_2 , PtO₂, EtOH) of crude fisetinidin chloride (improved prep.; cf. Léon and Robinson, A., 1931, 1423) and subsequent acetylation (Ac_2O , C_5H_5N) gives the tetra-acetate, m.p. 184—186°, of dl-epiquebrachocatechin (7:3':4'-trihydroxyflavanol) (I), m.p. (hydrated) 93—96°. (I) is rearranged by aq. $KHCO_3$ at 115° into dl-quebrachocatechin (II) (tetra-acetate, m.p. 144—146°). The Ac_2 derivative of 3:4-dihydroxyacetophenone, m.p. 119—121° (lit. 114—116°) (improved prep.; cf. Stephen and Weizmann, J.C.S., 1914, 105, 1051), with β -resorcyaldehyde and HCl in cold EtOAc, followed by treatment with conc. HCl in MeOH, gives butinidin chloride; reduction and subsequent acetylation (as above) of this affords a little of the triacetate (III), m.p. 137—139°, of 7:3':4'-trihydroxyflavan (IV), m.p. 175—178° (to a red liquid). (IV) is obtained from (III) and EtOH-KOAc in H_2 ; hydrolysis with aq. Ba(OH)₂ gives a product contaminated with red amorphous material. (IV) is unstable in air or hot H_2O ; warm 2% HCl converts it into a red "phlobaphen," which when methylated and then oxidised gives veratric acid (V). When (II) is heated with dil. acid, an insol. condensation product [probably (VI)] is first produced; more

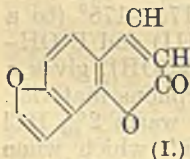


prolonged heating causes a secondary elimination of H_2O . The material extracted (Et_2O then $COMe_2$) from quebracho wood is separated into a small H_2O -sol. fraction, a main portion (A) sol. in hot but insol. in cold H_2O , and a small H_2O -insol. fraction. (A), which contains 1.2% OMe, gives m - $C_6H_4(OH)_2$ when heated with KOH; successive methylation (Me_2SO_4 , 55% KOH) and oxidation (aq. $KMnO_4$) affords (V). When (A) is heated with dil. acid, the C content increases (elimination of H_2O); acetylation of (VI) and (A) (and the other fractions) indicates that these are inter-related [and probably arise from (II) by a condensation which does not involve elimination of H_2O]. The OMe content of (A) is probably due to an admixed impurity.

H. B.

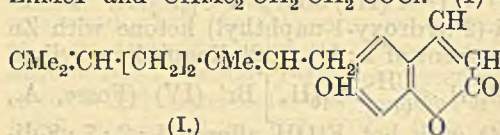
Natural coumarins. XI. Constitution of angelicin (from *Angelica archangelica*, L.). E. SPÄTH and O. PESTA. XII. Constitution of ostruthin (from *Imperatoria ostruthium*, E. SPÄTH and K. KLAGER (Ber., 1934, 67, [B], 853—858, 859—868).—XI. Extraction of angelica root with Et_2O , treatment of the extract with 3% KOH-EtOH, removal of Et_2O , and treatment of the residue

with 10% KOH-MeOH at 15–20° leads to the isolation of sterols and indifferent substances from which sitosterol, m.p. 135°, $[\alpha]_D^{25}$ –37.3° in CHCl₃, is isolated [this has been previously described as "angelicin," but it is proposed (see below) to use this designation for another compound]. The lactone fraction contains a compound, m.p. 83° (cf. Böcker *et al.*, A., 1911, i, 313), identified as osthol and *angelicin* (I), C₁₁H₆O₃, m.p. 138–139.5°, which does not contain OMe and does not afford [-CH₂·CO₂H]₂ (II) when oxidised. After hydrogenation (I) is oxidised by HNO₃ to H₂C₂O₄ and (II). Treatment of (I) with KOH-H₂O₂ yields H₂C₂O₄ and furan-2:3-dicarboxylic acid (Me₂ ester, m.p. 36.5°), whereas (I) is converted by KMnO₄-C₅H₅N and subsequent decarboxylation into umbelliferone. Treatment of osthol with NaOMe-Me₂SO₄ and subsequently with H₂O yields 2:4-dimethoxy-3- γ -methyl- Δ^{β} -butenylcinnamic acid, m.p. 82–84°, and an ester hydrolysed to an isomeric acid (III), m.p. 151–152°. Oxidation of (III) by KMnO₄ in dil. KOH followed by esterification of the product, hydrolysis, and successive treatment of the acid with SOCl₂ and NH₂Ph, leads to 2:4-dimethoxybenzene-1:3-dicarboxydianilide (IV), m.p. 206–207° (vac.). Since similar treatment of (I) leads to (IV), the annexed constitution is ascribed to it.



XII. Ostruthin (I), m.p. 119°, is C₁₉H₂₂O₃ (cf. Butenandt *et al.*, A., 1932, 751). It contains 1 OH (Zerevitinov), yields *m*-C₆H₄(OH)₂ when treated with molten KOH and styphnic acid when oxidised with HNO₃. Treatment of (I) with CH₂N₂ or Me₂SO₄ and NaOH leads to methylostruthin (II), m.p. 55–55.5°. (I) is hydrogenated (Pd-C in AcOH) to hexahydro-ostruthin (III), oxidised by HNO₃ to H₂C₂O₄ and [-CH₂·CO₂H]₂. With Me₂SO₄ and KOH followed by hydrolysis (II) gives an acid C₂₁H₂₈O₄ (IV), m.p. 99–100°. (II) is oxidised by CrO₃ in AcOH-H₂O to 7-methoxycoumarin-6-aldehyde, m.p. 252–254° (vac.) (the "methylostruthinaldehyde" of Butenandt *et al.*), the oxime of which is dehydrated by Ac₂O at 140–145° to 6-cyano-7-methoxycoumarin (V), m.p. 282° (vac.). Oxidation of (V) by KMnO₄ (=50) in C₅H₅N leads to 5-cyano-2-hydroxy-6-methoxybenzoic acid (VI), m.p. 236° (decomp.) (Me ester, m.p. 117–118°). When heated with Cu powder in quinoline at 235–240°, (VI) yields 4-hydroxy-2-methoxybenzonitrile, m.p. 156–157°, identical with the product obtained by the action of Ac₂O on 4-hydroxy-2-methoxybenzaloxime, m.p. 178°. 2-Hydroxy-4-methoxybenzaloxime, m.p. 136–138°, and 2-hydroxy-4-methoxybenzonitrile, m.p. 177–178°, are described. Oxidation of (IV) by KMnO₄ (=300) yields 4:6-dimethoxybenzene-1:3-dicarboxylic acid, m.p. 264° (vac., decomp.) (Me₂ ester, m.p. 152–152.5°). Oxidation of (I) by KMnO₄ in very dil. KOH affords H₂C₂O₄ and OH·CMe₂·CO₂H. (III) is transformed by H₂O₂-NaOH-H₂O into γ -dimethylnonoic acid (VII), b.p. 150–151°/10 mm., converted by SOCl₂ into the corresponding chloride, b.p. 115–120° (bath)/10 mm., and thence into the amide, m.p. 79–81° (vac.), identical with a specimen prepared from the acid obtained from tetrahydrogeraniol through

the corresponding bromide and nitrile. The *phenyl*- and *p*-*tolyl*-hydrazide of (VII) have m.p. 113–114° and m.p. 119.5–120°, respectively. Oxidation of (II) with CrO₃-AcOH gives COMe₂. β -Methyl- Δ^{β} -hepten- ζ -one, b.p. 170–173°/746 mm., obtained as by-product in the oxidation of (II) (see above) (semicarbazone, m.p. 137°, identical with that derived from citral) is hydrogenated (Pd-C in AcOH) to β -methylheptan- ζ -one; the semicarbazone, m.p. 156–157°, is identical with that of the ketone from ZnMeI and CHMe₂·CH₂·CH₂·COCl. (I) is therefore



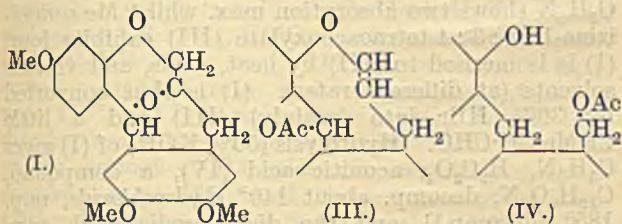
H. W.

Rotenone, the active constituent of *Derris* root. XIV–XVI. S. TAKEI, S. MIYAJIMA, and M. ŌNO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 1–24, and Mem. Coll. Agri. Kyoto, 1934, No. 31, 24 pp.).—Interaction of rotenone (I) in dil. NaOH-EtOH with O₂ at room temp. during 3 hr. affords rotenolone-I (II), m.p. 137–138°, and -II (III), m.p. 210° (oxime, m.p. 175°) (which are not converted into tubaic acid by boiling 5% EtOH-KOH), and a resin (IV). (II) and (III) afford dehydrorotenone with boiling 5% EtOH-H₂SO₄ during 3 hr. (also with Ac₂O containing C₅H₅N). Reduction (Pd-H₂) of (I) affords dihydro-, m.p. 214° (which is not further hydrogenated), and *dl*-isodihydro-rotenone, m.p. 206°. *iso*- and *dl*-*iso*-Dihydrorotenone are further reduced to tetrahydro-, m.p. 210°, and *dl*-tetrahydro-rotenone, m.p. 194°, respectively. (IV) affords with 2% cold NaOH in Et₂O *l*-deguelin, m.p. 166° converted by Pd-H₂ into the *dl*-form, which in EtOAc with Pd-H₂ gives dihydrodeguelin, m.p. 170°. Interaction of deguelin (VI) with alkali and O₂ affords deguelinol-I and -II [identical with tephrosin (A., 1931, 491) and isotephrosin (A., 1933, 69), respectively], which with EtOH-H₂SO₄ afford dehydrodeguelin, hydrolysed to deguelinic acid. Hydrolysis of (VI) affords β -tubaic acid, reduced (Pd-BaSO₄-H₂) in EtOAc to β -dihydrotubaic acid, m.p. 170°, identical with the acid prepared by hydrolysis of β -dihydrorotenone. *iso*Dihydrotubaic acid with conc. H₂SO₄ affords *iso*- β -dihydrotubaic acid, m.p. 193°. 4-Methoxytetrahydrotubaic acid (A., 1932, 400) at 200–230° during 0.5 hr. affords tetrahydrotubanolic Me₁ ether, b.p. 120°/7 mm., which gives with malic acid in hot conc. H₂SO₄ during a few min. 8-*iso*amyl-7-methoxycoumarin, m.p. 85–85.5° (cf. A., 1932, 751; 1933, 614). The physiological properties of some of these substances are investigated.

J. L. D.

Brazilin and hæmatoxylin. XIV. Trimethylallobrazilin. P. PFEIFFER and P. SCHNEIDER (J. pr. Chem., 1934, [ii], 140, 9–28).—Reduction of trimethylbrazilone with Na-Hg in EtOH-AcOH affords α -trimethylalhydrobrazilone, trimethylbrazilinol, β -trimethylbrazilipinacone, α - (I) and the stereoisomeric β - (II), m.p. 143.5°, -trimethylallobrazilin, C₁₉H₂₀O₅ (no OH or CO), and the compounds C₁₉H₂₀O₆ + H₂O and anhyd., m.p. 110°, C₁₉H₁₈O₆, m.p. 165°, and C₁₉H₂₀O₅, m.p. 220°. Warm EtOH (+1 drop NaOH) effects quant. conversion of (II)

into (I). With $\text{Ac}_2\text{O}-\text{NaOAc}$ (I) or (II) yields an unsaturated *Ac* derivative (III), m.p. 121—122.5°,



(saturated oily H_2 -derivative), and readily hydrolysed by dil. AcOH back to (I). Reduction ($\text{Pd}-\text{BaSO}_4-\text{H}_2$ in AcOH) of (I) gives (with pinacolonic rearrangement)

2-hydroxy-2'-acetonyl-4 : 4' : 5' : 5'-trimethyl-diphenylmethane (IV) [*Ac* derivative, m.p. 102°; *oxime*, m.p. 193°; *Me ether* (V), m.p. 91° (*oxime*, m.p. 118°)], oxidised by 30% $\text{H}_2\text{O}_2-\text{KOH}-\text{MeOH}$ to 2-hydroxy-4 : 4' : 5' : 5'-trimethyl-diphenylmethane-2'-carboxylic acid, m.p. 222—224° [*Ac* derivative, m.p. 99°, *Me ester*, m.p. 159° [*Me ether*, m.p. 118°, by similar oxidation of (V)]] identical (and giving identical derivatives) with the product obtained by $\text{Zn}-\text{AcOH}$ reduction of 6-(2-hydroxy-4-methoxybenzoyl)-3 : 4-dimethoxybenzoic acid (Perkin, J.C.S., 1907, 91, 1079; prep. improved). J. W. B.

Thiophen derivatives. IV. I. J. RINKES (Rec. trav. chim., 1934, [iv], 53, 643—651; cf. this vol., 81).—The ease of nitration of thiophen is intermediate between that of C_6H_6 and furan. The NO_2 -group directs a second NO_2 to the "m"-position, unless overwhelmed by the "o"-directing power of the S. 3-Nitro-2-methylthiophen, KMnO_4 , and MgSO_4 in hot COMe_2 give a poor yield of 3-nitrothiophen-2-carboxylic acid, m.p. 137° (*Me ester*, m.p. 56°). *Me* thiophen-3-carboxylate and HNO_3 (*d* 1.51) in Ac_2O at -10° give *Me* 5-nitrothiophen-3-carboxylate, m.p. 81° (corresponding acid, m.p. 147°). Oxidation of 2-nitro-3-methylthiophen affords 2-nitrothiophen-3-carboxylic acid, m.p. 155—156°. Tetraiodothiophen, m.p. 199°, with $\text{Al}-\text{Hg}$ in $\text{Et}_2\text{O}-\text{EtOH}$ (3 : 1) yields 3-iodothiophen, b.p. 77°/11 mm., affording the 2- NO_2 -derivative, m.p. 140—141°, with $\text{HNO}_3-\text{Ac}_2\text{O}$. 2-Iodothiophen with HNO_3-AcOH in Ac_2O gives much 5-, m.p. 75°, and a little 3- NO_2 -derivative (I), m.p. 131°, both giving with $\text{HNO}_3-\text{H}_2\text{SO}_4$ the 3 : 5-(NO_2)₂-derivative, m.p. 145°. 2-Iodo-5-acetothienone, when oxidised first with alkaline KMnO_4 and then with H_2O_2 , gives 3-iodothiophen-5-carboxylic acid, m.p. 133—134° (lit. 131°), affording with $\text{HNO}_3-\text{Ac}_2\text{O}$ (I) and 2-iodo-3-nitrothiophen-5-carboxylic acid, m.p. 201° (*Me ester*, m.p. 118°). Me_2 thiophen-3 : 5-dicarboxylate (modified prep.) with HNO_3 (*d* 1.51)- H_2SO_4 at -10° gives a NO_2 -derivative, m.p. 94°. R. S. C.

Stereoisomerism of disulphoxides and related substances. IX. Disulphoxides in the thianthren series. H. BAW, G. M. BENNETT, and (Miss) P. DEARNS (J.C.S., 1934, 680—684).—Oxidation of 2 : 6-dimethoxythianthren with HNO_3 (*d* 1.2) affords α - (Fries *et al.*, A., 1915, i, 155) (main product if $\text{H}_2\text{O}_2-\text{AcOH}$ is used) and the stereoisomeric β -disulphoxide, m.p. 198—200°. Similarly 2 : 6-dimethylthianthren ($\text{H}_2\text{O}_2-\text{AcOH}$ at 80°) gives α -, m.p. 202.5°

(corr.), and β - (?cis-), m.p. 174° (corr.), -disulphoxides, and (with 3 atoms of O) a trioxide (sulphone sulphoxide), m.p. 223°, reduced by $\text{Zn}-\text{AcOH}$ to the monosulphone, m.p. 170—171°. 2 : 6-Dichlorothianthren (I), m.p. 186° (corr.), prepared by the action of oleum on $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{SH}$, is also the only pure product isolated from the condensation of PhCl , S_2Cl_2 , and AlCl_3 (Fries *et al.*, A., 1909, i, 406), isolation of the 2 : 7-isomeride being doubtful. Oxidation of (I) affords α -, m.p. 313° (corr.), and β -, m.p. 267.5° (corr.), -disulphoxides, a monosulphoxide, m.p. 235—237° (decomp.), and a trioxide, reduced to a monosulphone, m.p. 215°; with excess of CrO_3-AcOH a disulphone, m.p. 305° (corr.), is obtained. J. W. B.

Salts of pyridine-like amines. P. PFEIFFER and F. TAPPERMANN (J. pr. Chem., 1934, [ii], 140, 29—38).—By determining the solubility of various amines (*B*) in H_2O and in dil. acids (*A*) the mol. proportions of *A* and *B* in the salt formed in solution is ascertained. α - and β -Naphthoquinoline, $\beta\text{-C}_{10}\text{H}_7\text{-NH}_2$, and $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ in dil. HCl or HNO_3 all give *A* : *B* = approx. 1 : 1 (ions BH^+ and X^-), but *o*- (improved prep.) and *m*-phenanthroline with aq. HNO_3 and *d*-camphor- β -sulphonic acid give *A* : *B* = approx. 1 : 2 (ions $[\text{B}\cdot\text{H}\cdot\text{B}]^+$ and X^-), of which type *di*-*o*-phenanthroline mononitrate, + H_2O and anhyd., is isolated. J. W. B.

Metal pyridine methylnitroamine complexes. T. L. DAVIS and C. W. OU (J. Amer. Chem. Soc., 1934, 56, 1064—1065).—The prep. and properties of $\text{Co}(\text{NMe}\cdot\text{NO}_2)_2$, $2\text{C}_5\text{H}_5\text{N}$, $\text{Cu}(\text{NMe}\cdot\text{NO}_2)_2$, 1, 2, and 3 $\text{C}_5\text{H}_5\text{N}$, and $\text{Ni}(\text{NMe}\cdot\text{NO}_2)_2$, $2\text{C}_5\text{H}_5\text{N}$ are described and their dissociation pressures have been measured at 20°. The Ni compound decomposes at low temp. E. S. H.

Reduction of nitriles. R. GRAF (J. pr. Chem., 1934, [ii], 140, 39—45).—Addition of aq. KOH in H_2 to PhCN and $\text{Cr}(\text{OAc})_2$ in EtOH effects reduction to $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ and $\text{NH}(\text{CH}_2\text{Ph})_2$. Similarly MeCN affords NH_2Et , 2-cyanopyridine gives 2-pyridylmethylamine, b.p. 78—80°/12 mm. [*dihydrochloride*, m.p. 209—212° (decomp.)], and 2 : 6-dichloro-4-cyanopyridine gives 2 : 6-dichloro-4-pyridylmethylamine (Wibaut *et al.*, A., 1933, 282) (*hydrochloride*, decomp., 275—277°; *Bz* derivative, m.p. 61—63°). J. W. B.

Oximes of 3-benzoyl-6-phenylpyridine. H. NIENBURG (Ber., 1934, 67, [B], 874—878).—Treatment of 3-benzoyl-6-phenylpyridine with $\text{NH}_2\text{OH}\cdot\text{HCl}$ (I) and NaOH in $\text{EtOH}-\text{H}_2\text{O}$ yields in addition to the β -ketoxime (II), m.p. 183—184° (cf. Benary *et al.*, A., 1924, i, 872), the α -ketoxime (III), m.p. 160° after softening at 157° when slowly heated. The proportion of (II) to (III) appears to depend on the purity of (I). Partial isomerisation of (III) to (II) occurs under the action of PCl_5 in Et_2O . The Beckmann transformation of (III) therefore yields *BzOH*, NH_2Ph , 6-phenylpyridine-3-carboxylic acid, m.p. 229° (*loc. cit.*), and 3-amino-6-phenylpyridine, m.p. 105—106° [*aurichloride*, m.p. 169° (decomp.)]; *Ac*, m.p. 148—149°, and *Bz*, m.p. 201°, derivatives. (II) or (III) does not appear to yield internal complex salts with Co, Ni, or Fe salts. H. W.

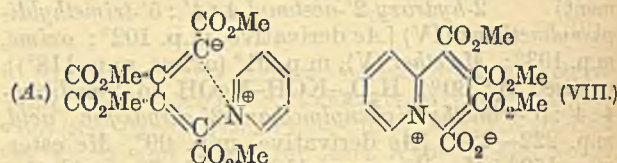
Manganohalides of pyridine and quinoline. F. S. TAYLOR (J.C.S., 1934, 699—701).—The light green compound, m.p. 152—155° (decomp.), given the formula $MnCl_4 \cdot 2C_5H_5N$ by Reitzenstein (A., 1899, i, 160) is actually $(C_5H_5NH)_2MnCl_4$ (I) and is also obtained from $MnCl_2 \cdot HCl \cdot C_5H_5N$, by Pincussohn's method [A., 1897, i, 540, this author's compound being a mixture of (I) and a pink compound $MnCl_2 \cdot C_5H_5NHCl + H_2O$], or from hot solutions of anhyd. $MnCl_2$ and dry $C_5H_5N \cdot HCl$ in abs. EtOH. The corresponding $(C_5H_5NH)_2MnBr_4$, m.p. 173° (Meyer *et al.*, A., 1900, ii, 77), is also light green, the colour of these salts being due to $MnCl_4$. By similar methods from quinolinium halides (QH_X) are obtained the compounds $(QH)MnCl_3 + 2H_2O$ and $+H_2O$, $(QH)_2MnCl_4$, and $(QH)_2MnBr_4 + 2H_2O$ and anhyd. J. W. B.

Oxidation of homologous pyridines and quinolines by selenium dioxide. M. HENZE (Ber., 1934, 67, [B], 750—753).—The base is heated with SeO_2 in presence of xylene or amyl alcohol (to moderate the sudden violence of the action) for several hr. at about 125°. Pure C_5H_5N is unaffected, whereas 2-methylpyridine affords pyridine-2-carboxylic acid with small amounts of pyridine-2-aldehyde. 3-Methyl- and 2:6-dimethyl-pyridine give the corresponding acids. Quinoline is unaffected, whereas 2-methylquinoline affords quinoline-2-carboxylic acid and -2-aldehyde (I), m.p. 71° (hydrate, m.p. 51°; *hydrazone*, m.p. 195—198° after subliming at 180°; *p-nitrophenylhydrazone*, m.p. 250°; condensation product, m.p. 261°, formed by action of KCN). Use of a smaller proportion of SeO_2 and lower temp. does not improve the yield of (I). Oxidation of 3-methyl-2-ethylquinoline affords mainly 3-methylquinoline-2-carboxylic acid, m.p. 142° (Cu salt). Application of the process to technical pyridines discloses the presence of higher homologues. H. W.

High-boiling bases from anthracene oil. S. K. GANGULI and P. C. GUHA (J. Indian Chem. Soc., 1934, 11, 197—206).—The fraction, b.p. 180—200°/30 mm., of the bases on oxidation to the carboxylic acids and esterification with $C_6H_4Ph \cdot CO \cdot CH_2Br$ gives the phenylphenacyl esters, m.p. 208°, 201°, 101°, the first being derived from quinoline- or isoquinoline-dicarboxylic acid (?). The fraction, b.p. 100—105°/2 mm., affords *picrates*, m.p. 230° (salt from $PtCl_4$, m.p. 220°; base, unknown *dimethylquinoline*), m.p. 181° (salt from $PtCl_4$, m.p. 202—203°; base, unknown *monomethylisoquinoline*), and m.p. 212° [salt from $PtCl_4$, m.p. 256—257° (decomp.); base, dimethylquinoline or -isoquinoline]; the fraction, b.p. 105—110°/2 mm., yields *picrates*, m.p. 201° (salt from $PtCl_4$, m.p. 207°; base, monomethylisoquinoline), m.p. 203° [salt from $PtCl_4$, m.p. 218° (decomp.); base, dimethylquinoline or -isoquinoline] and m.p. 198° [salt from $PtCl_4$, m.p. 234° (decomp.); base, 5:8-dimethylquinoline]. F. R. S.

Syntheses in the hydroaromatic series. XIX. Diene syntheses with heterocyclic nitrogen compounds. VII. Primary products in diene syntheses with pyridine, quinoline, and 2-methylquinoline. O. DIELS and K. ALDER [with W. FRIEDRICHSEN, PETERSEN, BRODERSEN, and KECH] (Annalen, 1934, 510, 87—128).—The labile red com-

pound (I), m.p. 124° (A., 1932, 1144) (improved prep. described), from Me acetylenedicarboxylate (II) and C_5H_5N shows two absorption max. whilst Me quinolizine-1:2:3:4-tetracarboxylate (III) exhibits four. (I) is isomerised to (III) by heat, acids, and various solvents (at different rates). (I) is thus converted by 30% HBr into (mainly) (III) and a little $CHMe \cdot CH \cdot CHO$. Hydrolysis (50% KOH) of (I) gives C_5H_5N , $H_2C_2O_4$, aconitic acid (IV), a compound, $C_{12}H_9O_6N$, decomp. about 140° [*hydrochloride*, m.p. 185° (decomp.)], and the dicarboxylic acid, m.p. 229°, previously described (*loc. cit.*; A., 1933, 1058). These results are explained by assigning structure (A) to (I); alkaline hydrolysis involves addition of



H_2O and the resulting pyridinium hydroxide decomposes to C_5H_5N and $CO_2Me \cdot CH \cdot C(CO_2Me) \cdot C(CO_2Me) \cdot C(OH) \cdot CO_2Me$ [which gives $H_2C_2O_4$ and (IV)]. (I) and CH_2N_2 in $Et_2O \cdot C_6H_6$ afford two isomeric adducts, $C_{18}H_{19}O_8N_3$, m.p. 159° (decomp.) (V) and 169° (decomp.) (VI), both hydrolysed (conc. HCl) to C_5H_5N and pyrazole-4:5-dicarboxylic acid (VII). (V) is reduced (H_2 , Pd, MeOH) to a tetrahydro-derivative, m.p. 189° [also hydrolysed (conc. HCl) to (VII)], whilst (VI) similarly gives a dihydro-derivative, m.p. 155°. (III) does not react with CH_2N_2 in C_6H_6 . (I) is oxidised by $Hg(OAc)_2$ in AcOH to the ester (VIII) (cf. A., 1933, 1058). (I) and Et azodicarboxylate in C_6H_6 give an adduct, $C_{23}H_{22}O_{12}N_3$, m.p. 170°, which absorbs 8H on reduction (H_2 , PtO_2 , AcOH); in MeOH, the Me methoxyquinolizine-1:2:3:4-tetracarboxylate, m.p. 160°, previously described (*loc. cit.*) results.

A labile adduct (IX), $C_{21}H_{19}O_8N$, m.p. 177°, yellow, is also obtained from quinoline and (II) in C_6H_6 . (IX) passes when heated to 195° or treated with conc. H_2SO_4 into the stable isomeride (X) (B, R=H), m.p. 234°, red. (IX) and (X) are oxidised [HNO_3 (d 1.17) or CrO_3] to a compound, $C_{18}H_{15}O_6N$, m.p. 129°, which is hydrolysed (50% KOH) to a substance $C_{14}H_9O_4N$, m.p. 259° (decomp.). (IX) is hydrolysed (16.6% KOH) to quinoline and $H_2C_2O_4$. Hydrolysis (24% KOH) of (X) gives 2-methylquinoline; with 5% KOH, a dicarboxylic acid, $C_{15}H_{11}O_4N$, m.p. 247°, results. (IX) and CH_2N_2 in C_6H_6 afford an adduct, $C_{22}H_{21}O_8N_3$, m.p. 153°, hydrolysed (conc. HCl) to quinoline and (VII); (X) does not react with CH_2N_2 . (IX) is reduced (H_2 , Pd, MeOH) to a dihydro-derivative, m.p. 151°, but (X) is similarly unaffected. (X) could not be reduced using H_2 , PtO_2 , and AcOH; (IX) gives a tetrahydro-derivative, m.p. 177°. The ester (B, R=OMe), m.p. 150°, is obtained from (IX) and Et azodicarboxylate in MeOH. Oxidation (H_2O_2 , AcOH) of (IX) or (X) gives quinoline-2-carboxylic acid 1-oxide, m.p. 171° (decomp.).

The stable red adduct (XI) (B, R=Me), m.p. 204°

(A., 1932, 1145) [from 2-methylquinoline and (II)], and Br in AcOH give a *tetrabromide*, m.p. 145—147° (decomp.), which is reduced (Zn dust, H₂O) to (XI), and converted by aq. HClO₄ into a *bromide perchlorate*, C₂₂H₂₁O₈NBrClO₄, m.p. 217° (previous decomp.), and by HCO₂H into a *dibromide*, C₂₂H₂₁O₈NBr₂, m.p. 145°. (XI) is reduced (H₂, PtO₂, AcOH) to a *dihydro-derivative* (XII), m.p. 164°, whilst the labile yellow adduct (XIII) (*loc. cit.*) similarly gives a *dihydro-*, m.p. 125°, and then a *tetrahydro-*, m.p. 170°, -derivative. (XI) is oxidised [HNO₃ (d 1.4) or CrO₃-AcOH] to a *base*, C₂₂H₂₁O₉N, m.p. 138° [*nitrate*, m.p. 215° (decomp.)], reduced (H₂, PtO₂, AcOH) to a *decahydro-derivative*, m.p. 181°. Hydrolysis (dil. MeOH-KOH) of (XII) gives an *acid*, C₂₁H₂₁O₈N, m.p. 247—248°, whilst (XI) is hydrolysed (conc. HCl) to a *tricarboxylic acid*, C₁₇H₁₃O₆N, H₂O, decomp. 245°, decarboxylated (CaO) to 2-methylquinoline. (XIII) and CH₂N₂ in C₆H₆ give an *adduct*, C₂₂H₂₃O₈N₃, m.p. 138°, hydrolysed (conc. HCl) to (VII). Structures are suggested for many of the above compounds. H. B.

Hypnotics containing the α -ethylpropyl group ; syntheses with higher esters of *p*-toluenesulphonic acid. D. L. TABERN and E. H. VOLWILER (J. Amer. Chem. Soc., 1934, 56, 1139—1142).—CHEt₂Br (I), b.p. 118.5—119.5°, prepared from CHEt₂OH (II) and HBr in H₂ at -25° to -20°, does not react with CHNa(CO₂Et)₂ in C₆H₆. *p*-C₆H₄MeSO₂Cl and (II) in C₆H₆-C₅H₅N give α -ethylpropyl *p*-toluenesulphonate (III), m.p. 32—35°, which decomposes on attempted distillation. CNaEt(CO₂Et)₂ and (III) in C₆H₆ afford Et ethyl- (α -ethylpropyl)malonate, b.p. 155—160°/45 mm., which condenses with CO(NH₂)₂ to give 5-ethyl-5- α -ethylpropylbarbituric acid (IV), m.p. 158.5—159.5°. CN·CHNa·CO₂Et and (I) in EtOH at 50—60° afford CN·CH(CHEt₂)·CO₂Et, ethylated (NaOEt, EtBr at 60°) to Et ethyl- (α -ethylpropyl)cyanoacetate, b.p. 150—155°/40 mm. This with CO(NH₂)₂ and NaOEt at 100—110° gives [after hydrolysis (dil. H₂SO₄)] (IV). 5-Methyl-, m.p. 204—206°, 5-*n*-propyl-, m.p. 130—133°, and 5-*n*-butyl-, m.p. 126—127°, -5- α -ethylpropylbarbituric acids are similarly prepared. 5-Allyl-5- α -ethylpropylbarbituric acid, m.p. 129—130°, is obtained from 5- α -ethylpropylbarbituric acid and allyl bromide in aq. KOH containing a little CuSO₄. 5-Methyl-, m.p. 180—182°, 5-ethyl-, m.p. 128—129°, 5-*n*-propyl-, m.p. 85—88°, 5-*n*-butyl-, m.p. 110—111°, and 5-allyl-, m.p. 98—100°, -5- α -methylbutylbarbituric acids are prepared by the malonate method; they are more efficient hypnotics than the corresponding α -ethylpropyl derivatives. H. B.

Preparation of dihydroimidazoles [glyoxalidines]. R. STOLLÉ, M. MERKLE, and F. HANUSCH (J. pr. Chem., 1934, [ii], 140, 59—64).—NH₂CPh·OEt (I) and CH₂Br·CH₂·NH₂·HBr (II) in EtOH-NaOEt give 2-phenyl-4 : 5-dihydroglyoxaline; NMc.CPh.OMe (in NaOMe-MeOH) affords the corresponding 1-Me derivative only as its *picrate*, sinters 116°, m.p. 130°, but with the *N*-Ac derivative of (I) only a *picrate*, m.p. 146° (not pure), is obtained. 2-Ethoxy- Δ^1 -homopiperidine and (II) in boiling EtOH give the *hydro-*

bromide, m.p. 182°, of the corresponding 2- β -bromoethylamino-derivative, (CH₂)₅<N<C-NH-CH₂-CH₂Br converted by NaOEt-EtOH into 1 : 2-pentamethylene-4 : 5-dihydroglyoxaline, b.p. 105—107°/15 mm. [*hydrobromide*, m.p. 172°; *picrate*, m.p. 166°; *urate* (base : acid = 2 : 1) and (1 : 1), m.p. 250°], hydrolysed by conc. HCl at 120° to the *dihydrochloride* of ϵ -(β -aminoethylamino)-*n*-hexoic acid [*picrate*, m.p. 147°; *dipicrate*, m.p. 144°, *di*(phenylurethane), m.p. 143°, and *dihydrochloride*, m.p. 196°, of its Me ester]. J. W. B.

Structure of monotrityluridine. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1934, 105, 419—430).—5-Monotrityluridine (I) with MeI and Ag₂O in COMe₂ gives a *Me*₃ derivative, m.p. 177—178°, [α]_D²⁵ +96.1°, which on hydrolysis (HCl in abs. MeOH) gives 2 : 3-dimethyluridine (II), m.p. 168—169°, and therefore has one Me in the uracil nucleus. In C₅H₅N (II) gives a (5)-*p*-toluenesulphonyl derivative which with NaI in COMe₂ gives the corresponding *I*-derivative, m.p. 94°, indicating the presence of the *p*-C₆H₄MeSO₂, and hence of the original trityl group, in the 5-position (cf. A., 1932, 254). (I) on the other hand gives a *di-p*-toluenesulphonate, [α]_D²⁵ +27.7°, hydrolysed by HCl-MeOH to 2 : 3-di-*p*-toluenesulphonyluridine, m.p. 199°, [α]_D²⁵ -26.6°, which is unaffected by NaI. Action of *p*-C₆H₄MeSO₂Cl in C₅H₅N on uridine gives 5-*chloro*-2 : 3-di-*p*-toluenesulphonyluridine, m.p. 170—171°, [α]_D²⁵ -9.3°, which with NaI gives the corresponding 5-*I*-compound, m.p. 160° (darkens 130°), [α]_D²⁵ -25°. Ditrityluridine has m.p. 223—224°, [α]_D²⁵ +91.4°. All vals. of [α]_D are in COMe₂. H. A. P.

Hydrogenation of cyclic ureides under elevated temperatures and pressures. I. 2-Keto-1 : 2 : 3 : 4-tetrahydropyrimidines. K. FOLKERS and T. B. JOHNSON (J. Amer. Chem. Soc., 1934, 56, 1180—1185).—Et 2-keto-4-phenyl-6-methylhexahydropyrimidine-5-carboxylate (I), m.p. 231.5—233.5° (all m.p. are corr.), and a small amount of an *isomeride*, m.p. 175—177.5°, are obtained by reduction [H₂ and Cu-Ba-Cr oxide at 200° (method *a*)] of the 1 : 2 : 3 : 4-tetrahydro-derivative (II). (I) is further reduced [H₂ and Ni at 145° (method *b*)] to Et 2-keto-4-cyclohexyl-6-methylhexahydropyrimidine-5-carboxylate (III), m.p. 181—184.5°, also obtained by reduction [H₂ and Ni at 175° (method *c*)] of (II). Reduction (method *b* or *Pt*) of (II) gives Et 2-keto-4-cyclohexyl-6-methyl-1 : 2 : 3 : 4-tetrahydropyrimidine-5-carboxylate (A., 1933, 515), reduced (method *a*) further to (III). Et 2-keto-4-styryl-6-methyl-1 : 2 : 3 : 4-tetrahydropyrimidine-5-carboxylate (IV) is reduced (H₂ and Cu-Ba-Cr oxide at 150°) to the 4- β -phenylethyl derivative, which is then reduced (method *a*) to Et 2-keto-4- β -phenylethyl-6-methylhexahydropyrimidine-5-carboxylate (V), m.p. 160.5—162.5°. Reduction (method *c*) of (IV) affords Et 2-keto-4- β -cyclohexylethyl-6-methylhexahydropyrimidine-5-carboxylate (VI), m.p. 147—152°. Hydrolysis (EtOH-NaOH) of (I), (III), (V), and (VI) gives 2-keto-4-phenyl- (VII), m.p. 256.5—258°, -4-cyclohexyl- (VIII), m.p. 290—291° (*loc. cit.*), -4- β -phenylethyl- (IX), m.p. 275—276°, and -4- β -cyclohexylethyl-, m.p. 296—297°, -6-methylhexahydro-

pyrimidine-5-carboxylic acid, respectively. Conversion of (VII) into the acid chloride with SOCl_2 and subsequent treatment with EtOH gives an *Et* ester, m.p. 178—179.5°, which differs from (I) and is hydrolysed to (VII); (VIII) similarly affords *Et* esters, m.p. 161—162° and 169—170.5°, whilst (IX) gives an *Et* ester, m.p. 145.5—147°. H. B.

Nucleic acids. IV. Constitution of the pyrimidine-nucleotides. H. BREDERECK (*Z. physiol. Chem.*, 1934, **224**, 79—85; cf. this vol., 394).—Deamination of cytidylic acid (I) with HNO_2 gives uridylic acid (II), isolated as the *dibrucine* salt, which with $\text{C}_5\text{H}_5\text{N}$ and CPh_3Cl affords triphenylmethyluridylic acid (III) as the *monobrucine* salt, m.p. from 184°, $[\alpha]_D^{20} -26.2^\circ$ in $\text{C}_5\text{H}_5\text{N}$. Elimination of brucine with aq. NH_3 gives the NH_4 salt, m.p. 165—170° (corr.), $[\alpha]_D^{20} +32.6^\circ$ in $\text{C}_5\text{H}_5\text{N}$. (III) yields *Na*, m.p. 170—175°, *Na*₂, m.p. 215—220°, and hence *Pb*, m.p. 211—213°, salts. Therefore in (I) and (II), H_3PO_4 is attached to a *sec. C*, probably atom 3. In confirmation, (I) and (II) do not yield complexes of greater dissociation const. with H_3BO_3 . J. H. B.

ψ -Bases. V. Reactions of *N*-methyl-dihydropyrazinium salts and their derivatives. J. G. ASTON, D. E. AILMAN, C. H. SCHEUERMANN, and J. M. KOCH (*J. Amer. Chem. Soc.*, 1934, **56**, 1163—1166).—When 6-hydroxy-1:2:2:5:5-pentamethyltetrahydropyrazine (I) is heated with MeOH and EtOH, 6-methoxy- (II), b.p. 111.5—113°/27 mm., and 6-ethoxy-, b.p. 118—122°/30 mm., -1:2:2:5:5-pentamethyltetrahydropyrazine, respectively, are formed. (II) is also obtained from 1:2:2:5:5-pentamethyl-dihydropyrazinium iodide (III) and MeOH-NaOMe. 1:2:2:3:5:5:6-Heptamethyl-dihydropyrazinium iodide (IV) and MeOH-NaOMe similarly give 1:2:2:3:5:5-hexamethyl-6-methylenetetrahydropyrazine (V) (*A.*, 1931, 367). (I) or (III) and $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ afford 6-benzyl-1:2:2:5:5-pentamethyltetrahydropyrazine, b.p. 192—194°/30 mm., m.p. 63—64°. 6-Phenyl-1:2:2:5:5-pentamethyl-, b.p. 146.5—154°/10 mm., and 1:2:2:5:5:6-hexamethyl-, b.p. 72—74°/13 mm., -tetrahydropyrazines are obtained from (I) and MgPhBr and MgMeI , respectively. (IV) and $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ give 6-benzyl-1:2:2:3:5:5:6-heptamethyltetrahydropyrazine, b.p. 210—213°/28 mm. (V) does not form additive compounds with Grignard reagents. (I) is converted by boiling *N*-NaOH into 2:2:5:5-tetramethyl-dihydropyrazine. H. B.

Reduction of isatin. A. WAHL (*Chim. et Ind.*, 1934, **31**, Spec. No., 761—762).—In cold MeOH isatin (I) is almost quantitatively reduced by H_2S to dithioisatin, $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_2\text{S}_2$, which, slowly in cold but more rapidly in warm $\text{C}_5\text{H}_5\text{N}$, passes into *isoindigotin* and *oxindole*. Interaction of (I) and H_2S in $\text{C}_5\text{H}_5\text{N}$ affords isatan, $\text{NH}\langle\text{C}_6\text{H}_4\rangle\text{C}(\text{OH})\text{-CH}\langle\text{C}_6\text{H}_4\rangle\text{NH}$, m.p. about 260° (slight decomp.). H. W.

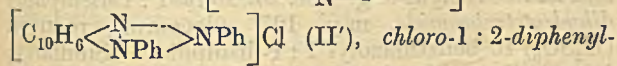
1-Arylindazoles. W. BORSCHKE and K. DIACONT (*Annalen*, 1934, **510**, 287—297).— PhN_2Cl and 2:4-(NO_2)₂ $\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ in MeOH + NaOAc at 0° give

the phenylhydrazone, m.p. 182—183°, of Me 2:4-dinitrophenylglyoxylate (I), which with *N*-NaOH in boiling MeOH loses HNO_2 and affords 6-nitro-1-phenylindazole-3-carboxylic acid, m.p. 272° (decomp.). This at 280° gives 6-nitro-1-phenylindazole, m.p. 120°, reduced (H_2 , Pd-C, MeOH) to 6-amino-1-phenylindazole (II), m.p. 150°. Reduction (H_2 , Pd-C, MeOH) of 6-iodo-1-phenylindazole, m.p. 156°, affords 1-phenylindazole, m.p. 78° (*platinichloride*, m.p. 170°), also prepared by diazotisation of (II) and subsequent treatment with EtOH or H_3PO_2 . The *o*-tolylhydrazone, m.p. 185°, *anisylhydrazone*, m.p. 170°, *o*- (III), m.p. 185°, *m*-, m.p. 198—199°, and *p*-, m.p. 228—230°, -nitrophenylhydrazones, *o*-carboxyphenylhydrazone (IV), m.p. 262°, β -naphthylhydrazone, m.p. 170°, and 1-phenyl-6-indazolylhydrazone, m.p. 232°, of (I) are similarly prepared. (III) and (IV) are hydrolysed (as above) to the *o*-nitrophenylhydrazone, m.p. 205°, and *o*-carboxyphenylhydrazone, m.p. 225° (decomp.), respectively, of 2:4-dinitrophenylglyoxylic acid; the remainder give 6-nitro-1-*o*-tolyl-, m.p. 245° (decomp.), -1-*anisyl*-, m.p. 265° (decomp.), -1-*m*-, m.p. 248° (decomp.), and -1-*p*-, m.p. 275° (decomp.), -nitrophenyl-, -1- β -naphthyl-, m.p. 268° (decomp.), and -1-1'-phenyl-6'-indazolyl-, m.p. 295°, -indazole-3-carboxylic acids. 6-Nitro-1-*anisyl*-, m.p. 128—130°, -1-*m*-nitrophenyl-, m.p. 163°, -1- β -naphthyl-, m.p. 135°, and -1-1'-phenyl-6'-indazolyl-, m.p. 185°, -indazoles are prepared by thermal decomp. of the appropriate acids. Me 2-nitro-4-carbomethoxyphenylacetate (V) (improved prep.; cf. *A.*, 1917, i, 15) and PhN_2Cl similarly give the phenylhydrazone, m.p. 177°, of Me 2-nitro-4-carbomethoxyphenylglyoxylate; hydrolysis affords the phenylhydrazone, m.p. 208° (decomp.), of 2-nitro-4-carboxyphenylglyoxylic acid. (V) and *isoamyl* nitrite in MeOH-NaOMe give the *oxime*, m.p. 208° (decomp.), of Me 2-nitro-4-carboxyphenylglyoxylate, hydrolysed (*N*-NaOH) to 3-hydroxy-4-cyanobenzoic acid, m.p. > 300° (formed by way of benzisooxazole-3:6-dicarboxylic acid). Me 4-nitro-2-carbomethoxyphenylacetate and PhN_2Cl in MeOH + NaOAc give Me 7-nitro-1-keto-2-phenyl-1:2-dihydroquinoxaline-4-carboxylate, m.p. 218° [free acid, m.p. 238° (decomp.)]; with *isoamyl* nitrite, the *Me*₁ ester, m.p. 145—150° (decomp.), of 4-nitro-2-carboxyphenylglyoximic acid results. H. B.

Photochemical behaviour of lactoflavin; model experiments in the quinoxaline series. R. KUHN and F. BAR (*Ber.*, 1934, **67**, [B], 898—904).—Irradiation of 2-tetrahydroxybutylquinoxaline (I) [obtained by condensation of *d*-glucose with $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$] in alkaline solution with ultra-violet light results in the production of quinoxaline, with consequent disappearance of optical activity. (I) gives an *Ac*₄ derivative, m.p. 120°, $[\alpha]_D^{20} -29.3^\circ$ in $\text{C}_5\text{H}_5\text{N}$. There is therefore a very close resemblance between (I) and lactoflavin (II) which does not extend to their behaviour towards acids and oxidising agents. Possibly 3 C of the tetrahydroxybutyl group are photochemically removed, leaving an aldehyde which by Cannizzaro change passes into the acid which suffers decarboxylation. (II) resembles alloxazine (III), $\text{C}_6\text{H}_4\langle\text{N}:\text{C}\text{-NH}\text{-CO}\text{N}:\text{C}\text{-CO}\text{-NH}\rangle$, and dimethylalloxazine (IV) in

forming a bright red, radical-like intermediate when reduced by Zn, Sn, or Na-Hg in strongly acid solution. This change is not shown by quinoxaline (V) or 2-hydroxyquinoxaline (VI), and appears to be due to the presence of the intact, alkali-labile pyrimidine ring. The absorption spectra of (II) and (III) are very closely similar. Alkaline hydrolysis of (III) leads to 2-hydroxyquinoxaline-3-carboxylic acid, m.p. 265° (decomp.) when rapidly heated, which passes by loss of CO₂ into (VI). (IV) can be obtained by the action of MeI on the Ag salt of (III), thus establishing the presence of two active H in (III). (IV) in EtOH has marked blue fluorescence reversibly discharged by mineral acid and slowly destroyed by alkali by hydrolytic fission of the pyrimidine ring. (V) and benzimidazole (VII) in H₂O do not fluoresce, whereas 2:3-dihydroxyquinoxaline in dil. Na₂CO₃ has strong blue fluorescence destroyed by Na₂S₂O₄, but recurring in presence of air. Pentahydroxy-*n*-amylbenzimidazole, m.p. 246° (decomp.), $[\alpha]_D^{20} +50^\circ$ in C₅H₅N, +52.5° in AcOH, yields very little (VII) when irradiated; its Ac₆ derivative has m.p. 179°, $[\alpha]_D^{20} +75^\circ$ in C₅H₅N. H. W.

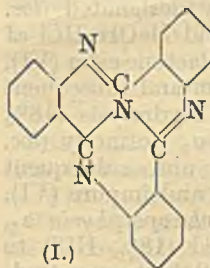
Action of acid chlorides on aryl- β -naphthylamineazo-compounds. F. KROLLPEFFER [with G. WOLF and H. WALBRECHT] (Ber., 1934, 67, [B], 908—916).—The action of boiling BzCl on benzeneazophenyl- β -naphthylamine (I) in presence or absence of air gives 2:3-diphenyl- $\alpha\beta$ -naphtha-1:2:3-triazolium chloride, $[C_{10}H_6 \langle \overset{+}{N}Ph \rangle NPh]Cl$ (II) or



$\alpha\beta$ -naphthimidazole, m.p. 207.5—208.5°, *ang.*-naphthaphenazine (III), NPhBz (IV), NPhBz, α -C₁₀H₇·NPhBz, C₆H₆, HCl, and N₂. At room temp. little (I) is produced, the main products being (III) and (IV). BzCl and (I) in presence of C₅H₅N yield the Bz derivative, m.p. 186—187°, (II), and Cl-compounds. Formation of (II) is not induced by AcCl, CH₂Ph·COCl, or POCl₃, and only to a slight extent by SOCl₂ or crotonyl chloride. With *p*-C₆H₄Me·SO₂Cl in boiling xylene the *p*-toluenesulphonate, m.p. 225—226°, of (II) is formed in 70% yield. SO₂Cl₂ reacts violently with (I) with elimination of PhN₂Cl and formation of substitution or additive products of Cl and C₁₀H₇·NPh, but not of (II). Cautious chlorination of (I) in AcOH leads to elimination of PhN₂Cl. SO₂Cl₂ and NPh₂ smoothly afford 2:4:2':4'-tetra-chlorodiphenylamine, m.p. 141—142°. HNO₃ converts (I) into tetranitrodiphenylamine, m.p. 254—255° (decomp.), also obtained from *p*-chlorobenzeneazo-phenyl- β -naphthylamine, whereas benzeneazo-*p*-chlorophenyl- β -naphthylamine gives a mixture of di- and tri-nitrated *p*-chlorophenyl- β -naphthylamines. Non-cryst. benzeneazodi-*p*-tolylamine is converted by non-cryst. benzeneazodi-*p*-tolylamine into 2-phenyl-3-*p*-tolyl-6-methylbenzo-1:2:3-triazolium picrate, m.p. 156.5—157.5° [corresponding chloride, m.p. 196—197° (decomp.) after softening]. H. W.

Tricycloquinazoline. I. J. KOZAK and A. KALMUS (Bull. Acad. Polonaise, 1933, A, 532—539).—By heating *o*-NH₂·C₆H₄·CHO with NH₄Cl at 230° a 22%

yield of tricycloquinazoline (I), m.p. 308—310°, is obtained. With AcOH-HNO₃ (*d* 1.32) (I) gives a (NO₂)₃-decomp. > 360°, and with AcOH-HNO₃ (*d* 1.52) a (NO₂)₆-derivative. With Cl₂ in AcOH solution (I) gives a Cl₃-derivative, m.p. 344—346° [(NO₂)₃-derivative, decomp. 400°], and with hot 60% oleum, a hexasulphonic acid as its Ba salt. Oxidation of (I) with Na₂Cr₂O₇-H₂SO₄ gives 4-hydroxyquinazoline (*picrate*, m.p. 204°). J. W. B.

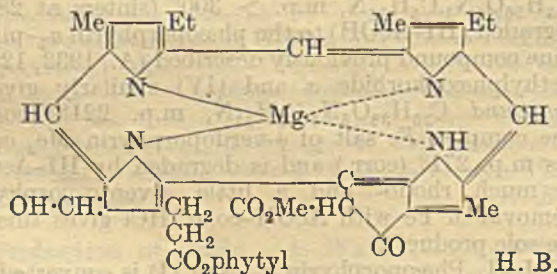


Chlorophyll. XLV. Partial synthesis of chlorophyllide *a*. H. FISCHER and G. SPIELBERGER. **XLVI. Oxidation products of phæophorbide *a* and phæoporphyrin *a*₅.** H. FISCHER, J. HECKMAIER, and T. SCHERER. **XLVII. Chlorophyll *b*.** **IV. Conversion of rhodinoporphyrin *g*₇ into rhodinoporphyrin *g*₈.** H. FISCHER and S. BREITNER (Annalen, 1934, 510, 156—169, 169—182, 183—192).—XLV. A mixture of Et₂O-MgEtBr and Mg is evaporated to dryness in absence of O₂ and the residue treated successively with EtOH, C₅H₅N, and methylphæophorbide *a* (in C₅H₅N); a chlorophyllide (I), C₃₇H₃₈O₅N₄Mg (which appears to consist largely of ethylchlorophyllide), is thus obtained. (I) gives a good phase test and is degraded (HI) to phæoporphyrin *a*₅ ester. (I) (in EtOH) absorbs approx. 1 mol. of O₂; subsequent degradation (HI) gives 10-ethoxyphæoporphyrin *a*₅ (II), phæoporphyrin *a*₇ Et ester, and some rhodoporphyrin. Allomerisation of (I) with benzoquinone-EtOH in N₂ and subsequent reduction (HI) gives (II). Ethylchlorophyllide *a*, C₃₇H₃₈O₅N₄Mg, prepared [as (I)] from ethylphæophorbide *a*, is converted by MeOH-CH₂N₂ into chlorin *e* ester. Contrary to Stoll and Wiedemann (this vol., 308) phæophorbide *a* (III) is readily oximated in C₅H₅N; the resulting oxime is identical with that obtained (*loc. cit.*) by hydrolysis of methylphæophorbide *a*-oxime. (III) and piperidine (IV) in MeOH give a compound C₃₅H₃₆O₅N₄·C₅H₁₁N, m.p. > 300° (sinters at 280°), degraded (HI-AcOH) to the phæoporphyrin *a*₅-piperidine compound previously described (A., 1932, 1264). Methylphæophorbide *a* and (IV) similarly give a compound C₃₆H₃₈O₅N₄·C₅H₁₁N, m.p. 221° (corr.). The complex Fe salt of ψ -verdoporphyrin Me₂ ester has m.p. 271° (corr.) and is degraded by HI-AcOH to much rhodo- and a little ψ -verdo-porphyrin (removal of Fe with AcOH-conc. HCl gives this as the sole product).

XLVI. Phæoporphyrin *a*₅ ester (I) is converted by EtOH-I into 10-ethoxyphæoporphyrin *a*₅ [previously described (A., 1932, 757) as a phæoporphyrin *a*₆ ester], hydrolysed (18% HCl) to phæoporphyrin *a*₇ Et ether (II), m.p. 287° [formerly designated (*loc. cit.*) isophæoporphyrin *a*₇] (*Cu* salt), which is degraded (HI-AcOH) to rhodoporphyrin ester (III). Hydrolysis (hot 30% MeOH-KOH) of (II) gives (III); in the cold, rhodoporphyrin- γ -carboxylic acid and its anhydride result. (II) is converted by conc. H₂SO₄ into (after esterification with CH₂N₂) phæoporphyrin *a*₇ Me₃ ester (IV) [formerly described (this vol., 421)

as *allophæoporphyrin a₇* ester]. 10-Hydroxyphæoporphyrin *a₅* ester (V) [previously designated (*loc. cit.*) neophæoporphyrin *a₆* ester] and MeOH-HCl at room temp. give chloroporphyrin *e₇* lactone ester (VI), m.p. 284°, converted by 30% oleum and subsequent esterification (CH₂N₂) into (IV). Hydrolysis (18% HCl) of 10-acetoxyp hæoporphyrin *a₅* [formerly (*loc. cit.*) acetylneophæoporphyrin *a₆*] and subsequent esterification (CH₂N₂) affords (IV) and impure (VI). (I) and MeOH-I give 10-methoxyphæoporphyrin *a₅*, C₃₇H₄₀O₆N₄, m.p. 254°, hydrolysed (18% HCl) to phæoporphyrin *a₇*, Me ether. 10-Acetoxymethylphæoporphorbid (VII) is hydrolysed (cold 80% H₂SO₄ or MeOH-HCl) to 10-hydroxymethylphæoporphorbid (VIII), m.p. 280°, degraded (HI-AcOH) to (V). (VII) and a little HI in AcOH give oxoacetoxyp hæoporphyrin *a₅*, C₃₈H₃₈O₈N₄, m.p. 307°. (VII) is converted by Et₂O-CH₂N₂ in MeOH-C₅H₅N into a chlorin, m.p. 261°. (VIII) and 10% NaOH in Et₂O afford an unstable chlorin, converted by CH₂N₂ into phæopurpurin 7; (V) similarly gives (IV), whilst (VI) furnishes chloroporphyrin *e₅*. Prolonged treatment of phæoporphyrin *a₇*, Me₁ ester with Et₂O-CH₂N₂ in MeOH-C₅H₅N gives [by way of (IV)] phæoporphyrin *a₇*, Me₂ ester Me ether. Structures are suggested for several of the above compounds.

XLVII. The complex Fe salt of rhodinporphyrin *g₇*, Me₃ ester (I) (A., 1933, 1173) and HI (*d* 1.96) in AcOH and air give rhodinporphyrin *g₈* (II), C₃₇H₄₀O₈N₄, m.p. 285° (decomp.), which contains 3 CO₂Me and 1 CO₂H [which probably arises from the CO group of (I)] and is esterified (CH₂N₂) to the Me₄ ester, m.p. 268°. (II) does not give an oxime. Rhodin *g* Me₃ ester is similarly converted into rhodinporphyrin *g₇*. (II) and 48% HBr at 220° afford a porphyrin, which with Br in AcOH gives a compound, C₃₀H₃₀O₂N₄Br₂, resembling pyroporphyrin. Prolonged treatment of phæoporphorbid *b* with Et₂O-25% HCl gives rhodin *g* (III) and pyrop hæoporphorbid *b*. (III) is converted by MeOH-NaOMe in C₅H₅N-N₂H₄ at 137–142° into phylloporphyrin. Chlorophyll *b* is formulated as follows (the position of the :CH-OH is uncertain):



Synthesis of indolenines. II. 3-Methyl-3-β-oxyethylindolenine. T. HOSHINO (Proc. Imp. Acad. Tokyo, 1934, 10, 159–160).—Et β-indolylacetate has m.p. 42–43° (cf. A., 1931, 97). The Grignard compound from tryptophan, m.p. 58–59° (*loc. cit.*), with MeI gives 4-methyl-1:2-dihydrofuroindolenine (I), m.p. 42–43°, b.p. 110–112°/2 mm. The Ac, m.p. 74–75°, and Bz, m.p. 151–152°, derivatives are insol. in dil. acids, and regenerate (I)

with MeOH-KOH. Hence it is concluded that (I) has the annexed structure. A. A. L.

Condensation of 1 : 8-naphthalyl chloride with *m*-ethylcarbonatodimethylaniline. W. R. BROWN and F. A. MASON (J.C.S., 1934, 651–653; cf. A., 1933, 1173).—*m*-OH·C₆H₄·NMe₂ and ClCO₂Et in 10% NaOH at 0° afford *m*-ethylcarbonatodimethylaniline, b.p. 160–164°/13 mm., which with 1 : 8-naphthalyl chloride at 0° in C₂H₂Cl₄ containing AlCl₃ during 24 hr. gives 4' : 4''-bisdimethylamino-2' : 2''-diethylcarbonatodiphenyl-1 : 8-naphthalide (I), m.p. 253–254° (decomp.), converted by 10% NaOH into the rhodamine dye which dyes silk bluish-red. (I) when boiled with MeOH-Ba(OH)₂ and treated with H₂SO₄ affords 4' : 4''-bisdimethylamino-2'-hydroxy-2''-ethylcarbonatodiphenyl-1 : 8-naphthalide sulphate (?), m.p. 176–180° (decomp.), converted into (I) with NaOH.

J. L. D.

Formation and stability of polybromide derivatives of heterocyclic compounds. III. Bromination of *μ*-substituted benzthiazoles. M. A. S. CHAUDHRI, R. D. DESAI, and R. F. HUNTER (J. Indian Chem. Soc., 1934, 11, 249–256; cf. A., 1933, 284).—1-Chlorobenzthiazole (I) and Br in CHCl₃ give a dibromide (A., 1925, i, 987) with partly labile Br; H₂SO₃ gives (I). 1-Phenylbenzthiazole (II) similarly gives a dibromide, m.p. 119° [converted into (II) with H₂SO₃], and a tetrabromide (III) (cf. A., 1930, 483) which cannot have a thiazonium structure (cf. A., 1922, i, 576). 1-Thiolbenzthiazole (prep. described) and Br in CHCl₃ at 0° give benzthiazolyl 1 : 1-disulphide dihydrotetrabromide, m.p. 127° (decomp.), reduced (H₂SO₃) to benzthiazolyl 1 : 1-disulphide. Similarly, 1-methylbenzthiazole affords a hydrotribromide (IV), m.p. 70°, of 5(?)-bromo-1-methylbenzthiazole, m.p. 120°, into which it is converted by H₂SO₃. (IV) is probably formed by way of a true Br additive compound. 5-Bromo-1-aminobenzthiazole affords the hydrotribromide (golden-yellow) of 3 : 5-dibromo-1-aminobenzthiazole (which, when heated, gives Br and a product, m.p. > 285°), reduced (H₂SO₃) to 3 : 5-dibromo-1-aminobenzthiazole (V), m.p. 261°. 2 : 4-Dibromoaniline (prep. described) with CCl₄ in CHCl₃-H₂O affords 2 : 4-dibromophenylthiocarbimide, m.p. 63°, converted by boiling EtOH-NH₃ into 2 : 4-dibromophenylthiocarbimide, m.p. 171°, which with Br in boiling CHCl₃ followed by reduction with H₂SO₃ gives (V). (V) in CHCl₃ with Br affords a tetrabromide [converted into (V) by H₂SO₃], which when heated gives Br and a product, m.p. > 285°. Thiobenzanilide with Br in boiling CHCl₃ followed by reduction with H₂SO₃ affords a compound, m.p. 206°, and not 1-phenyl- or 5-bromo-1-phenyl-benzthiazole. J. L. D.

Aminobenzthiazoles. XIII. Nature of the bromo-additive compounds of 5-bromo-1-alkylaminobenzthiazoles obtained from *s-p*-bromophenylalkylthiocarbamides and bromine. M. ALIAZAM, R. F. HUNTER, and N. A. KHAN (J.C.S., 1934, 708–710).—The alleged dibromides of 5-bromo-1-alkyl(R)aminobenzthiazole (A., 1927, 263) are actually hydrodibromides. The following are described : R = Et (I), hydrodibromide, sinters 200–220°, m.p. 240–245° (decomp.), hydrotribromide, labile, m.p. 105°, and stable form, m.p. 140° (decomp.), and hydro-

pentabromide, m.p. 65°. Bromination of (I) with Br-CHCl_3 at 0° affords not the dibromide (*loc. cit.*), but the hydrotribromide of 3(?) : 5-dibromo-1-ethylamino-benzothiazole, m.p. 156—157° [contaminated with the Br-additive compound of (I)], which is obtained by reduction ($\text{SO}_2\text{-H}_2\text{SO}_3$); $\text{R}=\text{Pr}^a$, hydrobromide, m.p. 224°, and hydrodibromide, m.p. 146—147°; $\text{R}=\text{Bu}^a$, hydrobromide, m.p. 194°, and hydrodibromide, m.p. 150°; $\text{R}=\text{Bu}^b$, m.p. 147° (lit. 137°), hydrodibromide, m.p. 126—127°, and hydrotribromide, m.p. 80°; and $\text{R}=\text{isoamyl}$, m.p. 131—132°, hydrodibromide, m.p. 111—112°. J. W. B.

Synthesis of α -nicotine and α -nornicotine. L. C. CRAIG (J. Amer. Chem. Soc., 1934, 56, 1144—1147).—2-Cyanopyridine and $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{MgBr}$ give 2-pyridyl γ -ethoxypropyl ketone, b.p. 125°/5 mm., the oily oxime of which is reduced (Zn dust, EtOH-AcOH) to α -amino- δ -ethoxy- α -2-pyridylbutane, b.p. 132—135°/5 mm. De-ethylation (45% HBr at 140—150°) of this and dehydration of the resulting product with K_2CO_3 in Et_2O gives α -nornicotine (2-2'-pyridyl-pyrrolidine), b.p. 120°/12 mm. (picrate, m.p. 166°). Methylation (Me_2SO_4 , aq. NaOH) of α -p-toluene-sulphonamido- δ -ethoxy- α -2-pyridylbutane, m.p. 96°, and subsequent treatment with 46% HBr and K_2CO_3 (as above) gives α -nicotine (2-2'-pyridyl-1-methylpyrrolidine), b.p. 122°/25 mm. (picrate, m.p. 169°). Mg 2-pyrryl bromide and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CN}$ give 2-2'-pyrryl-4 : 5-dihydropyrrole, b.p. 144—145°/5 mm., reduced (Zn dust, EtOH-HCl) to (probably) 2-(2 : 5-dihydro-2-pyrryl)pyrrolidine, b.p. 135—140°/12 mm. (phenylthiocarbamate, m.p. 151°; picrate, m.p. 141°). Reduction (H_2 , PtO_2 , EtOH or AcOH) gives (probably) 2-pyrrylpyrrolidine, which decomposes in air to a tar. H. B.

Alkaloids of ergot. V. Nature of ergine. S. SMITH and G. M. THOMAS (J.C.S., 1934, 674—675).—Ergine (I) $\text{C}_{16}\text{H}_{17}\text{ON}_3$ (not $\text{C}_{17}\text{H}_{21}\text{ON}_3$ as in A., 1932, 526) is decomposed by alkalis (N-NaOH-MeOH ; 30% aq. NaOH) to 1 mol. of NH_3 and lysergic acid (II) (Jacobs *et al.*, this vol., 538) (sulphate, decomp. 245°). (I) is therefore the amide of (II). J. W. B.

Alkaloids of *Holarrhena antidysenterica*. II. Two new alkaloids from the bark and seeds of Indian *Holarrhena*, and their relationship to conessine. S. SIDDIQUI (J. Indian Chem. Soc., 1934, 11, 283—291; cf. A., 1933, 289).—Conessimine (I), isoconessimine (II), and conimine (III) are isolated (isolation described) from the seeds. (I) (1 mol.) [Bz derivative, m.p. 121° after softening at 115° (hydrochloride, m.p. 348° (decomp.) after softening at 233°); Ac derivative, an oil (hydrochloride, m.p. 278—280°; platinichloride, m.p. 254—256° (decomp.))] with CH_2O and HCO_2H (each 1.2 mols.) in boiling EtOH affords Me conessimine (conessine) (IV), m.p. 123—124°, identical with an authentic specimen. (II), m.p. 92°, $\alpha_D^{20} + 30.0^\circ$ in 1% EtOH [$+2\text{H}_2\text{O}$, m.p. 88—92°; hydrochloride, m.p. 335°; platinichloride, m.p. 285° (decomp.); hydriodide, m.p. 316°; picrate, m.p. 198—200° (decomp.) after sintering at 160°; hydrobromide, m.p. 344° (decomp.)], contains two NMe groups and one active H, and is methylated [as is (I)] to (IV). (III), m.p. 130°, $\alpha_D^{20} - 30^\circ$ in 1% EtOH [$+ \text{H}_2\text{O}$, m.p. 130°; hydrochloride, m.p. 318—320°

(decomp.); platinichloride, m.p. 296—298° (decomp.); picrate, m.p. 140—141° after sintering at 134°; hydriodide, m.p. 293°], contains one NMe and two active H atoms, and is methylated to (IV). (II) and (III) are different from conessidine and conkurchine (cf. A., 1933, 728). J. L. D.

Alkaloids of *Salsola Richteri*. II. Constitution of salsoline. A. OREKHOV and N. PROSKURNINA (Ber., 1934, 67, [B], 878—884; cf. A., 1933, 727).—The yield of alkaloid is doubled when EtOH is replaced by $\text{C}_2\text{H}_4\text{Cl}_2$ in the percolation process. The close relationship of salsoline (I) to the *Anhalonium* alkaloids, and particularly to carnegine, is stressed. (I) is transformed by excess of CH_2N_2 in MeOH into *O-methylsalsoline* (II), m.p. 117—119° [hydrochloride ($+2\text{H}_2\text{O}$ and anhyd.), m.p. 193—195°; N-Bz compound, m.p. 125—126°]. Treatment of (II) with MeI-MeOH or with $\text{Me}_2\text{SO}_4\text{-NaOH}$ followed by KI leads to *ON-dimethylsalsoline methiodide*, m.p. 206—208°, readily converted by boiling KOH-MeOH into the non-cryst. base, $\text{C}_{10}\text{H}_9(\text{OMe})_2\text{NMe}_2$, b.p. 153—155°/15 mm., which appears to yield a mixture of isomeric methiodides transformed by KOH-MeOH or $\text{Ag}_2\text{O-H}_2\text{O}$ into NMe_3 and 3 : 4-dimethoxy-1 : 2-divinylbenzene (III), m.p. 37—39°. Oxidation of (III) affords methahemipinic acid, m.p. 177—183° (ethylimide, m.p. 231—232°).

Treatment of (II) with CH_2O and HCO_2H leads to *ON-dimethylsalsoline*, identical with carnegine (Späth, A., 1929, 707). (I) is therefore A ($\text{R}=\text{Me}$ or H ; $\text{R}'=\text{H}$ or Me). H. W.

Cupreidine, a phenolic base derived from quinidine. R. LUDWICZAKÓWNA, J. SUZKO, and R. ZWIERSZCHOWSKI (Roczn. Chem., 1934, 14, 197—202).—Quinidine (I) when boiled with 60% H_2SO_4 loses Me to give cupreidine (II), m.p. 186—190° [methiodide, m.p. 277° (decomp.); dimethiodide, m.p. 248° (decomp.); Bz , m.p. 100—105°, 5-benzeneazo-, m.p. 145—146°, and 5-benzeneazosulphonic acid derivatives]. (II) regenerates (I) on methylation with CH_2N_2 . R. T.

[Action of hydrogen iodide on lupanine.] K. WINTERFELD and F. W. HOLSCHNEIDER (Ber., 1934, 67, [B], 778—779).—Examination of the action of red P and fuming HI on τ -lupanine confirms the production of β -lupanine. The small yield obtained by Clemo *et al.* (this vol., 538) is attributed to the difficulty of its isolation from the small amount of material used. H. W.

Identity of peganine with vasicine. E. SPÄTH and F. KUFFNER (Ber., 1934, 67, [B], 868—869; cf. this vol., 310).—Direct comparison of the bases, the hydrochlorides, chloroacetoxy-compounds, aurichlorides, platinichlorides, and picrates establishes the identity of peganine (I) with vasicine (II) (Ghose *et al.*, A., 1933, 77). Since the constitution of (I) is confirmed by the isolation of glycine by hydrolysis of Me 4-keto-3 : 4-dihydroquinazolyl-3-acetate, that of (II) must be amended. H. W.

Crystal forms and m.p. of opium alkaloids. L. KOFLER and A. KOFLER (Arch. Pharm., 1934, 272, 537—545).—Optical data are recorded for micro-

sublimates (photomicrographs) obtained from codeine, papaverine, thebaine, and narcotine. The m.p. of the sublimates are 155° (anhyd.), 147°, 194°, and 174°, respectively.
R. S. C.

Berbine derivatives. III. Application of amalgamated zinc to the reduction of dehydroberberinium salts to berbine derivatives and new derivatives of berbine. W. AWE [with H. ETZRODT] (Ber., 1934, 67, [B], 836—840; cf. A., 1933, 289).—For reduction of 1 g. of the base, 10 g. of Zn-Hg and 30 c.c. of 30% AcOH are used. The product is separated by addition of NH₃ to the resulting solution, followed by a single extraction with CHCl₃. The following examples are cited: berberinium sulphate to dihydrodeoxyberberine, m.p. 169—170°; palmatinium H sulphate to 16:17-dihydrodeoxypalmatine, m.p. 149—150°; jatrorrhizinium chloride to 16:17-dihydrodeoxyjatrorrhizine, m.p. 217—218°; 9-phenyldeoxyberberine and 9-phenylberberinium chloride to 9-phenyl-16:17-dihydrodeoxyberberine, m.p. 222°; 9-benzyl- to 9-benzyl-16:17-dihydrodeoxyberberine, m.p. 164°. The following *-deoxyberberines*, obtained from berberinium iodide and the requisite Grignard reagent, are reduced by Zn-Hg in presence of AcOH and 2N-H₂SO₄: 9-*o*-tolyl-, m.p. 188—189°, to 9-*o*-tolyl-16:17-dihydro-, m.p. 204°; 9-*m*-tolyl-, m.p. 194—195°, to 9-*m*-tolyl-16:17-dihydro-, m.p. 201°; 9-*p*-tolyl-, m.p. 168—169°, to 9-*p*-tolyl-16:17-dihydro-, m.p. 206°; 9-*o*-anisyl-, m.p. 181°, to 9-*o*-anisyl-16:17-dihydro-, m.p. 202°; 9- α -naphthyl-, m.p. 213—215°, to 9- α -naphthyl-16:17-dihydro-, m.p. 230°; 9-*veratryl*-, m.p. 191°, to 9-*veratryl*-16:17-dihydro-, m.p. 195°.

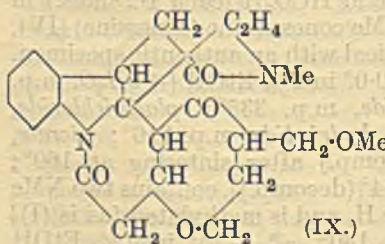
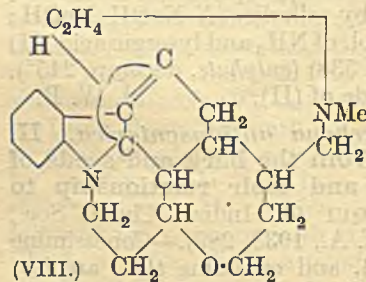
H. W.

Strychnine and brucine. XXV. Reduction of methylstrychnidinium salts by means of sodium amalgam in the presence of carbon dioxide. W. H. PERKIN, jun., R. ROBINSON, and J. C. SMITH. XXVI. Hofmann degradation of methylidihydrostrychnidinium-*A* carbonate. Isolation of a fourth isomeride of dihydrostrychnidine. O. ACHMATOWICZ and R. ROBINSON. XXVII. Methoxymethylchanodihydrostrychnone and the constitution of strychnidone. L. H. BRIGGS and R. ROBINSON. XXVIII. (a) Methoxymethylchanodihydrostrychnane. (b) Constitution of anhydrotetrahydromethylstrychnine-*K*⁵. (MISS) T. M. REYNOLDS and R. ROBINSON. XXIX. *N*(*b*)-Methylidihydrochanopseudostrychnine. B. K. BLOUNT and R. ROBINSON (J.C.S., 1934, 574—581, 581—590, 590—592, 592—595, 595—596).—XXV. The base *K*⁵ (A., 1932, 628) is contaminated by a compound of high C content which has not been entirely removed. Anhydrotetrahydromethylstrychnine-*K*⁵ on electrolytic reduction gives *dihydroanhydrotetrahydro-N*(*b*)-methylstrychnidine-*K*⁵, m.p. 112°. Strychnidine methosulphate is reduced (Na-Hg) in CO₂ to C₂₂H₃₀O₂N₂ (I), m.p. 235—236°, C₂₂H₂₈ON₂ (II), m.p. 142—143°, and C₂₂H₃₀ON₂ (III), m.p. 192—193°, methylstrychnidinium and methylneostrychnidinium salts remaining behind. (I) is *hydroxydihydro-N*(*b*)-methylchanodihydrostrychnidine- θ , (II) *N*(*b*)-methylchanodihydrostrychnidine- θ , and (III) *N*(*b*)-methylidihydrochanodihydrostrychnidine- θ . (I) and POCl₃ give (II), showing that (I) is the hydrate of (II). (II)

is reduced (Pd-H₂) to *N*(*b*)-methylidihydrochanodihydrostrychnidine-*A* (A., 1933, 406). (III) forms a *methiodide*, m.p. 270°. After separation of (I), (II), and (III) the residual bases have been reduced electrolytically to give (I) and *N*(*b*)-methylhexahydrostrychnidine- θ , b.p. 230—232°/42 mm. (*methiodide*, m.p. 278—280°). Reduction of *N*(*b*)-methylneostrychnidinium chloride affords (II) in small yield. The crude mixed bases on oxidation (KMnO₄) give an *acid*, C₂₂H₂₂O₅N₂ or C₂₂H₂₄O₅N₂, decomp. 210—220°; (II) similarly forms *oxy-N*(*b*)-methylchanodihydrostrychnidine- θ , m.p. 235—240°, a *substance*, m.p. 180°, and an *acid*, C₂₂H₂₄O₆N₂. The view is maintained that the ring fission occurs at different points in the formation of (II) and (III), and the significance of these results is discussed.

XXVI. By thermal decomp. *methylidihydrostrychnidinium-A* hydrogen carbonate and hydroxide each gives a mixture of five substances: dihydrostrychnidine-*A* (IV), a *des*-base, C₂₂H₂₈ON₂ (V), m.p. 143—144°, a substance C₂₃H₃₂O₂N₂ (VI), m.p. 220°, a substance C₂₂H₃₀O₂N₂ (VII), m.p. 158—159°, and a *des*-base C₂₂H₂₈ON₂ (VIII), m.p. 196—197°. (V) is identical with (II) as above; (VI) is methoxymethyltetrahydrostrychnidine; (VII) is *hydroxymethyltetrahydrostrychnidine hydrate*; (VIII) is *anhydromethylstrychnidinium-D* hydroxide (*methiodide*, m.p. 289—290°; *methochloride*, m.p. 308—310°). Oxidation of (V) and its dihydro-derivative gives AcOH, but the series *D* does not. Oxidation of (VIII) with KMnO₄ yields two *oxyanhydromethylstrychnidinium-D* hydroxides, m.p. 234—236°, and m.p. 162°. Catalytic hydrogenation of (VIII) affords *methylidihydrostrychnidinium-D* acetate, m.p. 307—308° [iodide (+H₂O), m.p. 317—318°; *chloride* (+H₂O), m.p. 318—319°]. The chloride decomposes to form *dihydrostrychnidine-D*, m.p. 197—199°. (VII) gives an *O-Ac* derivative, m.p. 254—255°, is methylated to the corresponding *OMe*-derivative, and on reduction (*P-HI*) yields an *isomeride* of methylidihydrostrychnidinium-*A* iodide, m.p. 225—228°. *N*(*b*)-*Ethylidihydrostrychnidinium-A* iodide, m.p. 345—350°, and *H* carbonate are described, the carbonate decomposing to give (IV). *Dihydrostrychnidine-E*, m.p. 254—255°, has been isolated in small yield during the prep. of *-A* salts. The constitution of the compounds is discussed and the structure (VIII) is suggested.

XXVII. Methoxymethylidihydrostrychnine is oxidised by Pb(OAc)₄ to *oxymethoxymethylidihydrostrychnine*, m.p. 210—243° (decomp.), and by perbenzoic acid to *methoxymethylchanodihydrostrychnone* (IX), m.p. 198—199° [*oxime*, m.p. 260—261° (decomp.); *P-*



nitrophenylhydrazone, m.p. 263°; benzylidene derivative, m.p. 235°]. (IX) and KOH give anhydrobismethoxymethylchanodihydrostrychnone, decomp. 268—273° (benzylidene derivative, m.p. 251—253°). "Strychnidonedisemicarbazone" (A., 1927, 888) consists of impure hydrazodicarbonamide. (IX) has the structure indicated.

XXVIII. Clemmensen reduction of (IX) leads to methoxymethylchanodihydrostrychnane, m.p. 160—161°; it is not a derivative of HCO·NH₂. Oxidation of anhydrotetrahydromethylstrychnine-*K*⁵ by KMnO₄ gives MeCHO and hence contains the group ·CH·CMe·CHMe. A series of strychnine derivatives has been examined for the occurrence of ·CMe groups by the Kuhn-Roth method: from these results strychnine does not contain ·CHMe and the C₂H₄ has the ethylene arrangement.

XXIX. Reduction of *N*(*b*)-methylchanopseudostrychnine (X) (Pt-H₂) yields *N*-methylidihydrochanopseudostrychnine, m.p. 296—297°, which forms a benzylidene derivative, m.p. 264—266°, but no derivative. The result favours the view that the second reactive CH₂ in (X) is in the system CO·C·C·CH₂.

F. R. S.

Preparation and investigation of cyclic polymethylenearsenic compounds. I. GORSKI, V. SCHPANSKI, and L. MULJAR (Ber., 1934, 67, [B], 730—735).—Methylcyclopentamethylenearsenic (improved prep.) is transformed by Cl₂ in CCl₄ into the corresponding dichloride, m.p. 153°, which at 95—101°/25 mm. affords chlorocyclopentamethylenearsenic (I), b.p. 89°/19 mm., m.p. 26—27°. (I) and NaOMe—MeOH afford cyclopentamethylenearsenic oxide, b.p. 118°/2 mm., oxidised by 25% H₂O₂ to cyclopentamethylenearsenic acid, [CH₂]₅>As(:O)·OH, m.p. 200.5—202°. Addition of dichloro-β-chlorovinylarsine to the Grignard compound from Mg and α-dibromopentane in Et₂O leads to cyclopentamethylene-β-chlorovinylarsine, b.p. 89—91°/5 mm., the dichloride, m.p. 121°, of which is decomposed by heat mainly into chloro-β-chlorovinyl-3-chloropentamethylenearsenic (II), b.p. 151—152°/5 mm., with smaller amounts of αε-dichloropentane (III), β-chlorovinylarsepidine, and (?) As β-chlorovinyl dichloride (IV). Non-cryst. As β-chlorovinyl-ε-chloropentamethylene trichloride, from (II) and Cl₂ in CCl₄, is decomposed by heat into (III) and (IV). H. W.

Reactions of phenylarsine with organic compounds of mercury, lead, and tin. A. N. NESMEJANOV and R. C. FRIEDLINA (Ber., 1934, 67, [B], 735—738).—The reaction between AsH₂Ph and HgPhCl, HgPh₂, PbPh₂Cl₂, PbPh₂I₂, PbPh₄, PbEt₄, SnPh₄, SnPh₂Et₂, SnEt₄, and SnEt₂Cl₂ has been examined. Hg compounds react at room temp., whereas Sn compounds require a temp. of 200—250°. In all cases of observed action Ph is eliminated as C₆H₆, and AsPh₂ after loss of H is converted into [AsPh]₂. Symmetrical aliphatic compounds react similarly, but with greater difficulty. [AsPh]₂ is obtained as such or in cases which require a very high temp. is decomposed into [AsPh₂]₂ and As. With mixed organometallic compounds, aryl is more readily eliminated than halogen. AsH₂Ph and SnEt₂Cl₂ do not react at 240—250°. H. W.

Arsonium compounds. J. PRAT (Bull. Soc. chim., 1933, [iv], 53, 1475—1488).—The solubility of four aromatic arsenic acids in HCl increases with increasing concn. of HCl, but suddenly falls at a definite concn., indicating compound formation. Using a special technique (detailed) to exclude atm. H₂O, there are obtained chlorides, [AsR(OH)₃]Cl, in which R = Ph, o- and p-C₆H₄Me, α-C₁₀H₇, p-C₆H₄·NH₂ (with the dichloride, +H₂O), C₆H₄·NHAc, the trichloride, [(C₆H₄·NH₂Cl)₂As(OH)₂]Cl + H₂O, and perchlorates of two types, [AsR(OH)₃]ClO₄ and [AsR(OH)₃]ClO₄·AsRO₃H₂, in which R = α-C₁₀H₇ (first type only), C₆H₄·NH₂, C₆H₄·NHAc, and 3-acetamido-4-hydroxyphenyl. R. S. C.

Use of camphor in cryoscopic determinations of mol. wt. of [organic] acids of arsenic. G. SCHUSTER (J. Pharm. Chim., 1934, [viii], 19, 497—498).—The mol. wt. of an insol. acid of As is determined in camphor after conversion into sol. thioglycollanilide. H. G. R.

Allylic rearrangement of lithium benzyl. H. GILMAN and F. BREUER (J. Amer. Chem. Soc., 1934, 56, 1127—1128).—o-Tolylcarbinol is obtained from LiCH₂Ph and CH₂O (gas) + N₂ in cold Et₂O. H. B.

Organo-metallic compounds. IV. Aromatic stannonic acids and their reactions. K. A. KOZESCHKOV and M. M. NADJ (Ber., 1934, 67, [B], 717—721; cf. A., 1929, 712; this vol., 423).—Sn(p-C₆H₄Me)₄ (I) and SnCl₄ (mol. ratio 0.083 : 0.25) at 210—215° yield Sn p-tolyl trichloride (II), b.p. 156—157°/23 mm. (I) and SnCl₄ (1 : 1) at 200—205° give Sn di-p-tolyl dichloride, m.p. 49—50°, converted into (II) by SnCl₄ at 210—215°. Sn(o-C₆H₄Me)₄ is transformed by SnCl₄ (1 : 3) into Sn o-tolyl trichloride (III), b.p. 154—158°/20 mm., or (mol. ratio 1 : 1) into Sn di-o-tolyl dichloride, m.p. 49—50°. (II) or (III) is transformed by HgCl₂ in boiling EtOH into o- (or p-)tolylmercurichloride. Cautious addition of 20% KOH to (III) in cold H₂O affords o-tolylstannonic acid (V), decomp. about 295°, readily displaced by CO₂ from its solutions in KOH. p-Tolylstannonic acid has similar properties. (III) and H₂S in H₂O give o-tolylthiostannonic thioanhydride, sol. in (NH₄)₂S. (IV) and HgO in boiling H₂O—EtOH afford Hg(o-C₆H₄Me)₂, m.p. 108°, and H₂SnO₃ quantitatively. Oxidation of (IV) by K₃Fe(CN)₆ in alkaline solution at room temp. gives PhMe and a small amount of o-C₆H₄Me·CN; exclusively inorg. compounds of Sn are produced. (II) and C₅H₅N in Et₂O give the substance, C₇H₇SnCl₃·2C₅H₅N. H. W.

Micro-hot-plate for protein hydrolysis. A. R. PATTON (Ind. Eng. Chem. [Anal.], 1934, 6, 201. E. S. H.

Preparation of gluco-protein. H. BIERRY (Compt. rend., 1934, 198, 1542—1543).—The complex which constitutes the glucoside linking (prep. described) decomposes about 195°, and has [α]_D²⁰ —4.5° in H₂O. J. L. D.

Structure and solubility of proteins. A. BONOT (J. Chim. phys., 1934, 31, 258—280).—Chiefly a review. The separation of serum-proteins by fractional pptn. with (NH₄)₂SO₄ is described. The solubility

data for serum-albumin in aq. $(\text{NH}_4)_2\text{SO}_4$ are consistent with a theory developed from the view that a protein is a mixture of different species with almost identical properties. J. G. A. G.

Combination of amino-acids and proteins in the solid state with gaseous acids and bases. E. J. CZARNETZKY and C. L. A. SCHMIDT (*J. Biol. Chem.*, 1934, **105**, 301—317).—From the phase-rule diagrams obtained by gasometric titrations the combining power of certain proteins for NH_3 is correlated with the CO_2H content; it is chemical in nature and takes place in stoichiometric proportions. The uptake of HCl is correlated with the content of $\epsilon\text{-NH}_2\text{-N}$ of lysine, NH-N of tryptophan, the guanidine group of arginine, the *tert.*- and NH-N of histidine, and the $\cdot\text{CO}\cdot\text{N}\cdot$ of proline and hydroxyproline. The changes in heat, free energy, and entropy with dissociation of the salts were determined. Similar data are given for the compounds of hexone bases with H_2S . C. G. A.

Copper ignition tubes. C. L. TSENG (*Sci. Quart. Nat. Univ. Peking*, 1934, **4**, 250).—An improved construction (cf. *A.*, 1933, 1022) is described.

W. R. B.

Determination of iodine in organic compounds. E. RUPP and O. LEMKE (*Z. anal. Chem.*, 1934, **97**, 180—181).—The substance is heated in a Kjeldahl flask with $\text{H}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_8 + \text{AgNO}_3$ (25 c.c. of 0.1*N* solution, evaporated down). Escaping HI or I vapours are trapped by moist Na_2SO_3 . Excess Ag is titrated back with KCNS. J. S. A.

Micro-determination of fluorine in organic substances. D. M. HUBBARD and A. L. HENNE (*J. Amer. Chem. Soc.*, 1934, **56**, 1078—1080).—The org. substance is decomposed over SiO_2 at 900° , and the SiF_4 produced is collected in H_2O or dil. aq. NaOH and titrated with $\text{Ce}(\text{NO}_3)_3$. The combustion tube is swept with H_2 to remove adsorbed SiF_4 . Cl may be determined simultaneously. E. S. H.

Gauge receiver for micro-methoxyl determination by Vieböck and Brecher's method. L. KAHOVEC (*Mikrochem.*, 1934, **14**, 341—342; cf. *A.*, 1931, 246).—An inexpensive attachment is described for addition to the condenser tube, in which the absorbing solution can be held and from which it can be transferred rapidly to the titration flask. J. W. S.

Analysis of mixtures of oxalic and citric acids by titration with ceric sulphate. J. A. WILKINSON, I. R. SIPHERD, E. I. FULMER, and L. M. CHRISTENSEN (*Ind. Eng. Chem. [Anal.]*, 1934, **6**, 161—163).—Citric (I) and oxalic acids in mixtures obtained by fermentation are separated as Pb salts. After recovery by H_2S , they are determined by (a) titration with NaOH and (b) oxidation in 0.01—0.02*N* solution by an excess of $\text{Ce}(\text{SO}_4)_2$ (modified prep.) in presence of a little H_2SO_4 at $90\text{--}95^\circ$ and back-titration of the excess. Oxidation of (I) to CO_2 and H_2O under these conditions is only 87.7% complete. R. S. C.

Application of drop reactions to the identification of organic compounds. I. Identification of the atomic groupings $>\text{C}\cdot\text{S}$ and $\text{C}\cdot\text{SH}$. F. FEIGL. II. Detection of carboxylic acids and their derivatives. F. FEIGL, V. ANGER, and O. FREHDEN. III. Detection of sulphonic acids.

F. FEIGL and V. ANGER (*Mikrochem.*, 1934, **15**, 1—8, 9—22, 23—24).—I. Reaction, with visible evolution of N_2 , between NaN_3 and I is catalysed by the CS and C·SH groups, but not by other types of org. S compounds. 1 drop of 3% NaN_3 in 0.1*N*-I suffices for the test. S dyes on cotton may be so detected, and vegetable fibres distinguished from (cysteine-containing) animal fibres.

II. Acid anhydrides dissolved in Et_2O are evaporated with a drop of 0.5% FeCl_3 in EtOH, saturated with $\text{NH}_2\text{OH}\cdot\text{HCl}$. Addition of H_2O gives a red to violet colour, due to the formation of a Fe hydroxamate (I). Esters are warmed with saturated $\text{NH}_2\text{OH}\cdot\text{HCl}$ + saturated KOH (both in EtOH), acidified with HCl, and dil. aq. FeCl_3 is added, giving (I). Thio-esters give yellow to red colorations. Acid chlorides (II) are treated with $\text{NH}_2\text{OH}\cdot\text{HCl} + \text{Na}_2\text{CO}_3$, then with HCl and FeCl_3 . Acids (1 drop) are converted into (II) by evaporating with 10 drops of SOCl_2 , then treated with KOH and NH_2OH as above.

III. $\text{R}\cdot\text{SO}_3\text{H}$ is converted into $\text{R}\cdot\text{SO}_2\text{Cl}$ by evaporation with SOCl_2 . 2 drops of saturated NH_2OH in EtOH + 1 drop of MeCHO are added, and the liquid is made alkaline with 5% aq. Na_2CO_3 . $\text{R}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{OH}$ is formed, which with MeCHO gives $\text{NHAc}\cdot\text{OH}$, detected by FeCl_3 as above. J. S. A.

2 : 4-Dinitrophenylhydrazine : reagent for carbonyl compounds. C. TORRES and S. BROSÁ (*Anal. Fis. Quim.*, 1933, **31**, 649—662).—2 : 4-Dinitrophenylhydrazine in dil. H_2SO_4 is not in general a useful reagent for α -hydroxycarbonyl compounds. Benzoin yields a 2 : 4-dinitrophenylhydrazone, m.p. $234\text{--}235^\circ$, but no osazone. Furoin and benzofuroin yield 2 : 4-dinitrophenylhydrazones, m.p. 223° (decomp.) and m.p. 170° , respectively, under certain conditions, but osazones cannot be isolated. 2 : 4-Dinitrophenylhydrazones are obtained from glucose and fructose [m.p. 238° (decomp.)] and from galactose [m.p. 216° (decomp.)]. Methods are described for the determination of COMe_2 or CH_2O in dil. aq. solution, of $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ (after oxidation to MeCHO by KMnO_4), and of $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ in pharmaceutical preps. of cinnamon. R. K. C.

Detection of aldehydes and ketones by means of micro-m.p. determination. R. FISCHER and A. MOOR (*Mikrochem.*, 1934, **15**, 74—86; cf. *A.*, 1933, 843).—M.p. data for the semicarbazones, *o*-, *m*-, and *p*-nitrophenylhydrazones and -nitrobenzhydrazones, semioxamazones, and thiosemicarbazones of a no. of aldehydes and ketones are given. J. S. A.

3 : 5-Dinitrobenzoylhydrazine as a reagent for the identification of aldehydes and ketones. P. P. T. SAH and T. S. MA (*J. Chinese Chem. Soc.*, 1934, **11**, 40—46).—Interaction of 3 : 5-dinitrobenzoylhydrazine (*A.*, 1907, i, 970) with aldehydes and ketones in cold 30% EtOH affords 3 : 5-dinitrobenzoylhydrazones. The following are described: *acet*-, m.p. $215\text{--}216^\circ$; *prop*-, m.p. $194\text{--}195^\circ$; *but*-, m.p. $171\text{--}172^\circ$; *isobut*-, m.p. $195\text{--}196^\circ$; *valer*-, m.p. $154\text{--}155^\circ$; *hex*-, m.p. $145\text{--}146^\circ$; *hept*-, m.p. $149\text{--}150^\circ$; *isohept*-, m.p. $127\text{--}129^\circ$; *oct*-, m.p. $106\text{--}107^\circ$; *non*-, m.p. $125\text{--}126^\circ$; *dec*-, m.p. $121\text{--}122^\circ$; *m-nitrobenz*-, m.p. $260\text{--}261^\circ$ (decomp.); *cinnam*-, m.p. $226\text{--}227^\circ$.

and *furfur-aldehyde-3:5-dinitrobenzoylhydrazone*, m.p. 234—235°. *Me hexyl ketone*-, m.p. 103—104°; *acetophenone*-, m.p. 228—229°; *benzophenone*-, m.p. 184—185°; *benzylideneacetone*-, m.p. 213—214°; *benzylideneacetophenone*-, m.p. 121—122°; *Et acetoacetate*-, m.p. 121—122°; *pyruvic acid*-, m.p. 166—167°; *lævulic acid-3:5-dinitrobenzoylhydrazone*, m.p. 161—162° (*Et*, m.p. 136—137°, and CH_2Ph , m.p. 117—118°, ester). J. L. D.

Semicarbazides. I. Phenylsemicarbazide as a reagent for the identification of aldehydes and ketones. P. P. T. SAH and T. S. MA (J. Chinese Chem. Soc., 1934, 11, 32—39).—Interaction of $NHPh \cdot CO \cdot NH \cdot NH_2$ (A., 1899, i, 137) with ketones and aldehydes in hot *EtOH* affords phenylsemicarbazones. The following are described: *acet*-, m.p. 151—152°; *prop*-, m.p. 130—131°; *n-but*-, m.p. 134—136°; *isobut*-, m.p. 133—134°; *n-valer*-, m.p. 126—127°; *n-hex*-, m.p. 135—136°; *n-hept*-, m.p. 134—135°; *isohept*-, m.p. 93—95°; *n-oct*-, m.p. 128—129°; *n-non*-, m.p. 131—132°; *n-dec*-, m.p. 108—110°; *m-nitrobenz*-, m.p. 194—195°, and *furfur-aldehyde-phenylsemicarbazone*, m.p. 180—181°. *Me hexyl ketone*-, m.p. 94—95°; *m-nitroacetophenone*-, m.p. 245—246°; *Et acetoacetate*-, m.p. 154°; *lævulic acid-phenylsemicarbazone*, m.p. 186—187° (*Et*, m.p. 118°, and CH_2Ph , m.p. 112—114°, ester). J. L. D.

Volumetric determination of amino-nitrogen in acetone solution. R. WOLFF and R. LAFRANCAISE (Bull. Soc. Chim. biol., 1934, 16, 419—423).—The influence of H_2O and *EtOH* on the volumetric determination of $NH_2 \cdot N$ in protein matter in $COMe_2$ is studied. A mixture of aq. $Co(NO_3)_2$, $K_2Cr_2O_7$, and a little $BaSO_4$ serves as a control for the end-point colour. A. L.

Determination of secondary in presence of primary and tertiary amines. A. NELIUBINA (Anilinokras. Prom., 1934, 4, 120—121).—0.3—3.5 g. of NH_2Ph and alkyylaniline mixture are dissolved in an excess (10%) of conc. HCl , 500 c.c. of H_2O are added, and the solution is titrated with 0.1N- $NaNO_2$ (at room temp. for $NHPhEt$ and at $> 5^\circ$ for $NHPhMe$). $NHPh_2$ is determined separately as picrate and $NPhEt_2$ is calc. by difference. R. T.

Determination of cholesterol.—See this vol., 822.

Microchemical detection of coumarin. A. KOFER and J. GEYR (Mikrochem., 1934, 15, 67—73).—Coumarin is best identified by microsublimation, followed by a micro-m.p. determination. Two crystalline modifications exist, a stable rhombic hemihedral form, m.p. 67°, and a metastable monoclinic form, m.p. 64°. J. S. A.

Reaction of cantharidin applicable to its colorimetric determination. G. DENIGÈS (Compt. rend., 1934, 198, 1783—1785).—A colorimetric method (sensitive to 0.01 mg.) for determining cantharidin, based on the intense brown colour produced when it is heated with 1 drop of 10% aq. CH_2O and a const. (4—5 c.c.) quantity of H_2SO_4 , is described. J. W. B.

Detection of nitrobenzene and phenol by formation of resorufin. P. W. DANCKWORTT (Z. anal. Chem., 1934, 27, 185—186; cf. this vol., 289).—The resorufin reaction is given also by other NO_2 -compounds, and is not sp. for $PhNO_2$. The sensitivity is increased by examination for fluorescence in ultraviolet light, and by extracting the dye with amyl alcohol. J. S. A.

Volumetric determination of 8-hydroxyquinoline. H. R. FLECK, F. J. GREENANE, and A. M. WARD (Analyst, 1934, 59, 325—328).—The end-point in the titration of 8-hydroxyquinoline may be obscured by the formation of a brown cloudiness. This may be avoided by adding CS_2 to the solution before adding KI . E. C. S.

Potentiometric determination of o-[8]-hydroxyquinoline by bromination. J. A. ATANASIU and A. J. VELCULESCU (Z. anal. Chem., 1934, 97, 102—106).—8-Hydroxyquinoline (or its salts) is brominated quantitatively to 5:7-dibromo-8-hydroxyquinoline in 10% HCl solution with 0.1N- $KBrO_3$ containing 5.246% KBr . Titration is best carried out at 50—55°; above 70°, reaction is not stoichiometric. Pt wire is used as indicator electrode. J. S. A.

Detection of nicotine. A. WENUSCH (Mitt. Österr. Tabakreg., 1932, 2, 2; Bied. Zentr., 1934, A, 4, 365—366).—The reaction between nicotine (I) and $p-NMe_2 \cdot C_6H_4 \cdot CHO$ is due to the presence of oxidation products of (I). The Schundelmeiser reaction with CH_2O and HNO_3 is unsatisfactory. The epichlorohydrin test is a suitable general reaction for C_5H_5N ring compounds and serves to distinguish (I) from coniine. A. G. P.

Microchemical contributions. L. ROSENTHALER (Mikrochem., 1934, 14, 363—368).—Quinine, diocaine, codeine, pantocaine, psicaine, stovaine, and strychnine salt solutions yield characteristic ppts. with solid $(NH_4)_2SiF_6$. Veramon (a 1:1 mol. mixture of pyramidone and pyramidone-veronal compound) gives barbituric acid-type ppts. with $Cu-C_5H_5N$ solution and with $(NH_4)_2HPO_4$, but not with $Pb(OAc)_2$, $TlOAc$, or I . With Br it gives the same long fine needle ppt. as pyramidone. Traces of $p-C_6H_4Cl \cdot CO_2H$ give characteristic ppts. with $AgNO_3$, $Hg(OAc)_2$, $UO_2(NO_3)_2$, and $Al(NO_3)_3$, and larger amounts also with $Ce(NO_3)_4$ and $La(NO_3)_3$. $o-C_6H_4Cl \cdot CO_2H$ also gives ppts. with $Hg(OAc)_2$, $AgNO_3$, and $Al(NO_3)_3$, but only when present in larger concn. $PhOH$, $p-C_6H_4Cl \cdot OH$, $\beta-C_{10}H_7 \cdot OH$, quinol, and salicylic acid give brown ppts., with I in KI . Phenolic acids give ppts. with $p-NMe_2 \cdot C_6H_4 \cdot NO$, but they are not characteristic without crystallographic examination. *iso*Propylantipyrine gives characteristic ppts. with $K_2Cr_2O_7$, $NaClO_4$, Reinecke's salt, $K[(NO_2)_4Co(NH_3)_2]$, and $KI+SnCl_2$. Ba can be distinguished from Ca and Sr by the needle ppt. it gives with 5% Na 5-chloro-5-nitrotoluenesulphonate. In presence of traces of Al , Mn , or Sn , $CoCl_2$ gives brown needles with a crystal of K_2CrO_4 . Alkaline-earth hydroxides give a characteristic blue to green ppt. with tannin. J. W. S.

Biochemistry.

Nature of the osmotic effect of solutions of non-electrolytes on the erythrocyte. M. H. JACOBS (Amer. J. Med. Sci., 1934, 187, 147).—The first change which takes place when ox erythrocytes are placed in sucrose solution is a reversible exchange of anions from the cell for OH⁻ from the solution; later there is an irreversible escape of salts into the solution.

CH. ABS.

Photo-electric determination of oxygen content and hæmoglobin concentration in hæmoglobin solutions and hæmolysed blood. K. KRAMER (Z. Biol., 1934, 95, 126—134).—The plot of the light absorption of a hæmoglobin (I) solution, measured by a photo-electric cell, against the % of O₂ in the (I) solution is a straight line for any given (I) concn. The validity of Beer's law for a wide range of (I) concn. is demonstrated and equations are derived whereby the O₂ content of a given (I) solution can be determined with an error of ± 0.1 vol.-%. H. D.

Determination of hæmoglobin in chicken blood. M. O. SCHULTZE and C. A. ELVEHJEM (J. Biol. Chem., 1934, 105, 253—257).—In a modified Newcomer method the blood is diluted with 0.4% aq. NH₃ and then acidified to yield a clear solution of acid hæmatin. The Fe content of chicken blood (I) gives only an approx. val. for its hæmoglobin content. Standard methods for determining O₂ capacity of blood cannot be used for (I) owing to gel formation.

A. E. O.

Blood-fats and hæmoglobin. Effect on chloroform fixation. L. SCOTTI-FOGLIENI (Compt. rend. Soc. Biol., 1933, 106, 1049—1053; Chem. Zentr., 1933, ii, 2844).—There is no relation between CHCl₃-solubility and the fat content of different kinds of animal blood, but there is a definite relation with the hæmoglobin content.

L. S. T.

Effect of hæmoglobin derivatives and hæmatin solution on the value of the chloroform solubility coefficient. L. SCOTTI-FOGLIENI (Compt. rend. Soc. Biol., 1933, 106, 1053—1055; Chem. Zentr., 1933, ii, 2844; cf. preceding abstract).—Cryst. hæmoglobin (I), methæmoglobin, and reduced (I) affect the CHCl₃ solubility ratios (II), in the same way as laked blood. The loss of respiratory function of the blood in no case reduces the CHCl₃ solubility, but it can result in a small increase. The (II) in a hæmatin solution is considerably > in slightly alkaline H₂O, but < in blood; hence it can be assumed that it is the prosthetic group in (I) which increases (II).

L. S. T.

Chloroform fixation in serum: sensitisation and the presence of small quantities of hæmoglobin. L. SCOTTI-FOGLIENI (Compt. rend. Soc. Biol., 1933, 106, 1055—1059; Chem. Zentr., 1933, ii, 2844).—The CHCl₃-solubility coeff. (I) of specially-prepared serum is practically the same as that of distilled H₂O, but sera containing small quantities (> 0.7—1.0%) of hæmoglobin (II) have vals. of (I) which equal those of blood. The (I) of diluted sera shows that the CHCl₃ solubility depends not only on dilution, but also on the physico-chemical condition of the (II) mol.

L. S. T.

Influence of physical factors on the lacto-gelatinisation of serum. W. KOPACZEWSKI (Compt. rend., 1934, 198, 1947—1950).—The rate of gelatinisation of serum (I) by lactic acid (II) is unaffected by coating the tube with paraffin, is greater if (I) is added to (II) than *vice versa*, decreases with age of (I) up to 144 hr., rises with temp., is accelerated by ultra-violet light, possibly by X-rays, by lowering the surface tension or increasing the viscosity of the solution, and by addition of neutral, insol. substances. The gel liquefies partly if heated to 45—50°, but resolidifies on cooling. It partly liquefies if dialysed or violently agitated.

R. S. C.

Alcoholic fission of serum-albumin. V. S. SADIKOV and V. A. VADOVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 185—187).—Serum-albumin with EtOH at 180° for 6 hr. yields 14.8% of the total N as NH₂-acids. Extraction with Et₂O and CHCl₃ followed by hydrolysis of the extract of the H₂O-sol. fraction (I) (82.5%) of the alcoholysate affords NH₂-N equiv. to 50—60% of the total N, but no (NH₂)₂-N. The H₂O-insol. fraction (II) on similar treatment yields no NH₂-N. Thus (I) and (II) contain, respectively, 40—50 and 100% of the total N as heterocyclic N. Hydrolysis of the corresponding residues does not increase the NH₂-N of (I), whilst that of (II) rises from 11.4 to 78.4% of the total N.

F. O. H.

Blood-sugar: physiological variation in non-diabetic patients. M. R. CASTEX and M. SCHEINGART (Compt. rend. Soc. Biol., 1933, 114, 78).—The fasting blood-sugar levels of 1000 patients, as determined by the Folin-Wu method, were 0.14—0.09% (in 450 cases > 0.10%). Of any 100 patients with levels below 0.10% 55 were female and 45 male; the levels of adolescents and of old people were slightly > the average, but the diurnal and seasonal variations in fasting patients were very small.

NUTR. ABS. (b)

Fermentation of blood-sugars. H. GIOVAMBATTISTA (Rev. fac. cienc. quim., La Plata, 1933, 8, ii, 47—63).—Identical results were obtained by the use of *Saccharomyces cerevisiae*, *S. ellipsoideus*, and *Zigosaccharomyces malli*. Whole blood deproteinised with H₂WO₄ gave higher vals. for non-fermentable reducing substances than that treated with Zn(OH)₂. For plasma or serum little difference was observed. Treatment with Hg(OAc)₂ or NaHCO₃ gave still lower vals.

CH. ABS.

Glycolysis of blood and its clinical interpretation. W. LOEWENSTEIN and B. BOTSTIBER (Klin. Woch., 1933, 12, 1402—1404).—Determinations of blood-sugar by the Hagedorn-Jensen method are subject to error if the blood is not heated in presence of the protein precipitants immediately on withdrawal. A diminution in reducing power, affecting the non-sugar reducing substances as well as the sugar, attains a max. in about 3 hr. When glycolysis is prevented, an increase in reduction may occur.

NUTR. ABS. (b)

Paradoxical hypoglycæmic reaction following glucose in hyperglycæmia due to hydrochloric

acid. G. LINO (Arch. Sci. biol., 1933, 19, 194—203).—Simultaneous injection of HCl and glucose (I) lowers blood-sugar (II). The increase in (II) induced by injection of HCl is not only arrested by subsequent injection of (I), but (II) falls below normal.

NUTR. ABS. (b)

Determination of sugar in 0.02 c.c. of blood (plasma etc.). F. RAPPAPORT and R. PISTNER (Mikrochem., 1934, 15, 111—113).—A modification of the Hagedorn-Jensen method is described.

J. S. A.

Blood-sugar. I. Determination. M. LORA Y TAMAYO (Anal. Fís. Quím., 1933, 31, 559—576).—1—2 c.c. of blood or plasma is deproteinised with Na_2WO_4 , filtered, and warmed with Fehling's solution (Folin formula); unreduced Cu is determined in the filtrate with KCN and AgNO_3 (A., 1930, 444). The method is accurate for >1 mg. of glucose (I). No (I) is found in blood or plasma treated with yeast, and after addition of (I) to such material the recovery is satisfactory.

R. K. C.

Sugar of cerebrospinal fluid. Determination by the cyanometric method. M. LORA Y TAMAYO (Anal. Fís. Quím., 1933, 31, 577—581).—The method described above (preceding abstract) is applied.

R. K. C.

Zinc hydroxide powder as a precipitant in a simplified procedure for the preparation of protein-free filtrate of blood. T. V. LETONOFF (Amer. J. Med. Sci., 1934, 187, 146).—Powdered $\text{Zn}(\text{OH})_2$ offers all the advantages of Somogyi's procedure, but eliminates the need for standardised solutions of NaOH and ZnSO_4 . Only traces of Zn appear in the filtrate. The true fermentable sugar level can be determined directly by alkaline Cu reagents. The neutral filtrates can be used for the determination of N fractions.

CH. ABS.

Relations between glucose, nitrogen, and cholesterol of blood. M. R. CASTEX and M. SCHEINGART (Compt. rend. Soc. Biol., 1933, 114, 745—746).—The blood-sugar level is not related to the level of cholesterol or N in the blood, although hyperglycæmia is often accompanied by a rise of these.

NUTR. ABS. (b)

Cholesterol of horse serum. D. BROCC-ROUSSEU, G. ROUSSEL, and G. GALLOT (Compt. rend. Soc. Biol., 1933, 114, 1075—1076).—The mean in 10 horses was 1.112 and in 13 mares 0.982%. It was increased in one horse after frequent bleeding from 1.047 to 1.103% and was also increased during gestation, the mean val. for 55 mares after 4 months being 1.201 and after 5—10 months 1.308%.

NUTR. ABS. (m)

Variations during the day and from day to day in total blood-fatty acids. J. M. MUÑOZ (Compt. rend. Soc. Biol., 1933, 114, 803—806).—In dogs on a standard diet there are rapid and irregular variations during the day and from day to day, and in summer the vals. are $>$ in autumn or winter.

NUTR. ABS. (m)

Origin of the lipæmia due to bleeding. F. ROSENTHAL, E. FRIEDLANDER, and R. KOHN (Arch. exp. Path. Pharm., 1934, 175, 343—352).—Repeated bleeding of rabbits produces a lipæmia (I) which is

not inhibited by rapid injection of plasma, erythrocytes, or whole blood, and appears to be due to cell destruction, and not to the removal of some blood constituent. (I), which does not increase the deposition of fat in the liver, occurs when the liver-glycogen is increased by insulin-glucose administration.

F. O. H.

Lipæmia after bleeding. U. STARUP (Z. physiol. Chem., 1934, 224, 116—120).—After cutting the medulla spinalis of rabbits above the seventh vertebra dorsalis (I) before successive bleedings, the lipæmia (II) is not so marked, and the lecithin/cholesterol quotient is not depressed so much as in ordinary (II) due to blood-letting, although (II) is not entirely prevented. Cutting below (I) has little or no effect.

J. H. B.

Determination of urea by urease methods in fluoride blood. C. F. M. ROSE (Brit. J. Exp. Path., 1933, 14, 339—342).—Caffeine Mg salicylate counteracts the inhibitory effect of F'. The principal mechanism involved is one of adsorption.

CH. ABS.

Detection and occurrence of preformed acetylcholine in blood and tissue. G. KAHLSON (Arch. exp. Path. Pharm., 1934, 175, 198—222).—In guinea-pigs, rabbits, cats, pigs, and man, the serum has the same content of free choline (I) as the erythrocytes; with oxen, the contents are 1:40. Of the intestine preps. of various animals, that of the mouse has the greatest sensitivity (0.05×10^{-6} g.) to acetylcholine (II). The frog's rectus abdominis muscle when sensitised with eserine is, however, suitable for the determination of (II) in tissue extracts. The blood (normal or hæmolysed with $\text{CCl}_3\text{-CO}_2\text{H}$ or Et_2O) of guinea-pigs, rabbits, cats, man, oxen, and horses does not contain (II) in detectable amounts (< 0.05 mg. per litre). With oxen, the (I) of the spleen is present totally as (II). The skeletal muscle of various animals is free from (II), whilst the large intestine contains considerable amounts. The formation and action of (II) in the body are discussed.

F. O. H.

Does normal blood contain chemically detectable amounts of acetylcholine? G. KAHLSON and R. RÖMER (Arch. exp. Path. Pharm., 1934, 175, 223—232).—Ox-blood was treated with EtOH and $\text{CCl}_3\text{-CO}_2\text{H}$, the filtrate conc. in vac., the residue re-pptd. with $\text{CCl}_3\text{-CO}_2\text{H}$, extracted with Et_2O , and finally pptd. with Reinecke acid. The ppt. contained the reineckates of choline and creatinine, but not that of acetylcholine (cf. A., 1932, 765; Dudley, J. Physiol., 1933, 79, 248).

F. O. H.

Blood-glutathione in old age. J. NITZULESCU and I. ORNSTEIN (Compt. rend. Soc. Biol., 1933, 114, 1134—1136).—The glutathione content of the blood varied from subject to subject, and with the limited nos. available could not be correlated either with age or sex.

NUTR. ABS. (b)

Blood-glutathione in Sebright cocks and hens. L. R. CHANTON and F. CARIDROIT (Compt. rend. Soc. Biol., 1933, 114, 893—894).—Whereas normally the blood-glutathione (I) of the cock is much $>$ that of the hen, in the Sebright cock, where plumage is the same as that of the hen, the (I) has the same val.

NUTR. ABS. (b)

Determination of reduced glutathione in blood. F. MURATA (Sei-i-kwai Med. J., 1932, 51, No. 10, 92—95).—In a modification of the Perlzweig-DeTRUE method, 3 c.c. of blood are added slowly and with shaking to 10 c.c. of H_2O , followed immediately by 10 c.c. of 1% $CCl_3 \cdot CO_2H$. The protein is then pptd. with 10 c.c. of 30% $CCl_3 \cdot CO_2H$. Rabbit's blood contains 0.0201—0.0264% (average 0.023%) of reduced glutathione. CH. ABS.

Non-protein-sulphur of blood and its relation to the adrenals. R. H. DE MEIO (Compt. rend. Soc. Biol., 1933, 114, 807—809).—There was no increase in blood-total S in dogs after removal of one adrenal, but after removal of the second the total S rose to 3—5 times normal. Neutral S was generally increased after removal of one or both glands. Non-protein-N was increased to a similar degree, suggesting that renal insufficiency was the cause. NUTR. ABS. (b)

Mineral balance of normal blood-serum in man. A. URBEANO (Compt. rend. Soc. Biol., 1933, 114, 467—469).—The excess of bases (Na, K, Ca, Mg) over acids (Cl, P) has been calc. Normal serum contains 59.3% of bases. Disease (pellagra, cancer) alters the val. NUTR. ABS. (m)

Mineral composition of the blood-serum of the horse and the pig. W. G. ROBINSON (Univ. Cambridge, Inst. Animal Pathol., Rep. Director, 1932—1933, 156—158).—Figures are given for the Ca, inorg. P, Na, and K contents. NUTR. ABS. (m)

Determination of non-protein-bound calcium in serum. G. TAUBMANN (Arch. exp. Path. Pharm., 1934, 175, 182—188).—Determinations of Ca in the filtrates from the pptn. of serum by phosphomolybdic acid and, to a smaller extent, by $CCl_3 \cdot CO_2H$ give erroneous results for the non-protein-bound Ca owing to adsorption of Ca by the ppt. Ultra-filtration is more difficult, but gives the most accurate results. F. O. H.

Determination of calcium in 0.2 c.c. of serum. F. RAPPAPORT and D. RAPPAPORT (Mikrochem., 1934, 15, 107—110).— CaC_2O_4 is pptd. by saturated aq. $(NH_4)_2C_2O_4$, and collected by centrifuging. The ppt. is dissolved in 4N- H_2SO_4 , excess of 0.001N-Ce $(SO_4)_2$ added, and titrated back with 0.001N- $Na_2S_2O_3$ after addition of KI. J. S. A.

Calcium and phosphorus contents of the blood-serum of healthy cattle. W. HIPPMAN (Diss., Hanover, 1930; Bied. Zentr., 1934, A, 4, 353—354).—Serum-Ca (I) and -P in males was somewhat > in females and in young > in older animals. Ca vals. for calves were especially high. After administration of Ca (I) increased over 90 hr., and subsequently declined (30 hr.) to normal. Following intravenous injection (I) attained max. val. in a few min. and reverted to normal in 15 min. A. G. P.

Concentration of calcium and phosphorus in the serum of children. L. SCHOENTHAL and D. K. LURIE (Amer. J. Dis. Children, 1933, 46, 1038—1044).—No change in the level of serum-Ca occurs in children from 5 to 16 years of age. The serum-P declines significantly beginning with the fifteenth year, especially in girls. Administration of viosterol (10—40

drops daily) or 1 quart. of milk does not regularly increase the levels. NUTR. ABS. (m)

Micro-determination of serum-calcium and -potassium. K. IN (J. Chosen Med. Assoc., 1933, 23, 1844—1852).—In a modification of the Kramer-Tisdall method excess of $KMnO_4$, then KI, are added, the liberated I being titrated with $Na_2S_2O_3$. CH. ABS.

Calcium content of cow's blood. II. (a) Calcium in the blood of parturient heifers; (b) effect of injections of parathyroid and irradiation; (c) some case reports of milk fever. W. L. LITTLE and E. C. V. MATTICK (Vet. Rec., 1933, 13, 1091—1097).—Heifers about parturition time show no change in total serum-Ca (I), but a lowering of diffusible serum-Ca (II) is noted at calving and is more pronounced 2—4 days *post partum*. Irradiation *ante partum* has no effect on (I). In milk fever (I) seldom exceeds 6 mg. and (II) is never above 3 mg. per 100 c.c. NUTR. ABS. (m)

Changes in blood-calcium and -potassium following intravenous injection of hypertonic salt solutions. G. DUCLOS and P. C. FABRE (Compt. rend. Soc. Biol., 1933, 114, 491—492).—A rise in alkali reserve and a fall (I) in plasma-Ca occur after intravenous injection of 30% NaCl into a dog, the vals. returning to normal within 1 hr. Since a diminution in Ca decreases the tonus of the splanchnic nerves, (I) accounts for the mechanism of the action of hypertonic NaCl in intestinal obstruction. NUTR. ABS. (m)

Calcium, potassium, phosphorus, and K : Ca ratio in the blood after partial removal of the liver. C. I. PARHON, H. DEREVICI, and M. DEREVICI (Compt. rend. Soc. Biol., 1933, 114, 67—68).—5—6 hr. after removal of about $\frac{2}{3}$ of the liver from guinea-pigs the serum-Ca tends to fall and the -P to rise. The K is diminished (average from 22.4 to 14.2 mg. per 100 c.c.). The average K : Ca ratio falls from 1.92 to 1.41. NUTR. ABS. (m)

Effect of injection of potassium and calcium on the K : Ca ratio in dogs. L. BALLIF and I. GHERSCOVICI (Compt. rend. Soc. Biol., 1933, 114, 324—325).—A progressive increase of blood-Ca and -P follows injection of KCl, the K : Ca ratio being increased up to three times the normal val. Injection of $CaCl_2$ generally leads to increased vals. for blood-K and -Ca, the K : Ca ratio being raised about 50%. NUTR. ABS. (m)

Alkali reserve and chloride ratio. M. CHATRON (Bull. Soc. Chim. biol., 1934, 16, 400—404).—The ratio corpuscle-Cl/plasma-Cl is important as a measure of the acid-base equilibrium in the blood, but it is elevated by increase of total Cl as well as by decrease of alkali reserve. W. O. K.

Blood-chlorine in afferent and efferent vessels of the chief viscera. L. BOTTIN (Compt. rend. Soc. Biol., 1933, 114, 1386—1389).—The blood-Cl of the dog, after fasting and immediately, or up to 2 hr., after a meal of 250 c.c. of milk, is unchanged in the afferent (I) and efferent vessels (II) of the liver, spleen, lungs, and brain. The (II) of the stomach, superior mesentery, and kidney, however, contain markedly

less Cl after a meal than the (I), the differences in vals. decreasing with fasting. NUTR. ABS. (b)

Physiological values of blood-iodine. T. LEIPERT (Biochem. Z., 1934, 270, 448—454).—The normal blood-I content (I) in man is $13 \pm 4 \times 10^{-6}$ g. per 100 c.c., no difference being detectable with age or sex. In woman (I) increases by > 100% at menstruation, and then quickly returns to normal, and in pregnancy gradually increases, the mean max. val. at the end being 31.5×10^{-6} g. per 100 c.c. The vals. fall rapidly during lactation. P. W. C.

Action of acid on the protein precursor of thrombin. A. FISCHER (Biochem. Z., 1934, 270, 235—249).—Traces of acid acting for a short time cause irreversible changes in the muscle-globulin [prothrombin (I)], the protein being no longer sol. in neutral salt solutions and the coagulation max. (II) being displaced from 5.3 to 9. Similar but not such large differences are obtained with serum- and plasma-globulins when (II) is displaced to the alkaline side, but only by 0.6—1.0 p_H . Mellanby's fibrinogen (III) is stable to acid so long as the amount added is not sufficient to cause any visible coagulation. Mixtures of (III) and (I) behave like pure (I). Heparin, but not nucleic acid, protects (I) against denaturation by acid, but cannot reverse the effect of acid. P. W. C.

Activation of prothrombin. A. FISCHER (Biochem. Z., 1934, 270, 250—260).—In the activation of prothrombin (I) by thrombokinase (II) a denaturation occurs which is non-sp. and can also be obtained by physical, chemical, and actinic reactions. This action results in the depression of the solubility of (I) at the neutral point. Heparin effects an inhibition of clotting by inhibition of the denaturation of (I) by (II). (II) exerts also a sp. action on the conversion of fibrinogen into fibrin. P. W. C.

Latent stage in blood-clotting. A. FISCHER (Biochem. Z., 1934, 270, 261—274).—The latent portion of the clotting process is investigated from the moment of addition of thrombokinase (I) to a plasma free from thrombin (II) to the end of the clotting process. Coagulation of plasma-protein in buffer solution poor in electrolytes at p_H 5 decreases as the latent period progresses, the increasing stability being due to the behaviour of fibrinogen (III). If (I) is added to pure solutions of (III) and prothrombin (IV), coagulation of (III) decreases and of (IV) increases, a mixture of (III) and (IV) behaving like whole plasma. Preheated (48—50°) plasma on treatment with (I) coagulates more quickly the larger is the pretreatment. In this process, denaturation occurs, (IV) and (II) proteins being so changed that after coupling with (I), (II) is immediately formed. P. W. C.

Identity of muscle- and blood-thrombin. A. FISCHER (Biochem. Z., 1934, 270, 275—280).—Muscle extract contains prothrombin (I) which can be converted into thrombin (II). Muscle- and plasma-globulin have the same physico-chemical properties as (I) and (II). Muscle-(II) and plasma-(II) can coagulate oxalate- and heparin-plasma. Muscle-(II) can also coagulate fibrinogen solution. Plasma-(I) can be replaced by muscle-(I). P. W. C.

Specific carbohydrates of blood-groups. K. FREUDENBERG and H. EICHEL (Annalen, 1934, 510, 240—248).—The substance (I) previously isolated (A., 1932, 1153) from the urine of individuals of blood-group A has C 43, H 6—6.5, and N 5.0—5.5% (of which about 10% is NH_2-N), $[\alpha] -5^\circ$ to $+5^\circ$, and contains about 9—10% of *N*-Ac group. The activity (retardation of hæmolysis) of (I) is destroyed by *N*-alkali at 60° (not at room temp. during 48 hr.), but is unaffected by pancreatic amylase, emulsin, diastase, takadiastase, papain, I in various solvents, H_2O_2 , aq. CH_2O , or conc. HCO_2H ; acetylation (Ac_2O , C_5H_5N) gives an inactive product, partial hydrolysis of which regenerates (I). Hydrolysis ($0.2N-H_2SO_4$) of (I) gives galactose (II) and an amino-hexose. Similar substances (possessing much smaller activities) are isolable from the urine of blood-groups O and B; both give (II) on hydrolysis. H. B.

Method of applying the precipitin test. C. C. HADDON (Analyst, 1934, 59, 342).—Drop preps. of antiserum and the experimental fluid are made on slides and examined microscopically. E. C. S.

Device for uniform lighting in precipitin tests. H. P. BEALE (Contr. Boyce Thompson Inst., 1904, 6, 165—166).

Action of light on visual purple. M. L. VERRIER (Compt. rend., 1934, 198, 1806—1808).—Although visual purple (I) (in retina films or in 4% solution in ox bile) of *Scyllium canicula*, L., and *Scorpena scrofa*, L. [poor in (I)], is decolorised by exposure to feeble illumination (65 c.p.), that of *Eledone moschata*, Leach, and *Julis giofredi*, Risso [rich in (I) and in melanin], is stable to intense illumination for prolonged periods [same absorption spectrum as with (I) from animals kept in dark]. Hence the alternate destruction and regeneration of (I) cannot be responsible for light-sensibility. J. W. B.

Extraction and determination of free choline [in tissues]. G. KARLSON (Arch. exp. Path. Pharm., 1934, 175, 189—197).—The tissue is extracted with EtOH or $COMe_2$, the extract evaporated in vac., and the residue freed from lecithin etc. by extraction with light petroleum. The residue of free choline (I) is then acetylated and the acetylcholine assayed by its action on the mouse's small intestine. Blood, serum, muscle, and intestine (guinea-pig, rabbit, man) have (I) contents of 0.28—1.17, 0.37—1.37, 0.30—1.13, and 4.27—7.28 mg. per 100 g., respectively. F. O. H.

Distribution of nitrogen in the muscular tissue of *Mullus barbatus*. L. G. BINI (Atti R. Accad. Lincei, 1934, [vi], 19, 111—115).—The % of the total N present in different forms are: amide 12.0, humin 2.5, arginine 9.4, histidine 15.9, lysine 7.45, non- NH_2 9.8, and NH_2 42.7. T. H. P.

Lipin content of the parathyroids in different animal species. C. I. PARHON and I. ORNSTEIN (Compt. rend. Soc. Biol., 1933, 114, 753—754).—The mean contents for 10 dogs, cats, and rabbits were 32.39, 57.91, and 60.63%, respectively.

NUTR. ABS. (m)

Fat content of the foetal lung. H. R. KANITZ (Virchow's Archiv, 1933, 291, 410—417).—The fat

content of the lungs during foetal life remains at first fairly const. (6th to 8th month, 15.7%), and then rises considerably until after birth (10th month 23.35%) and finally decreases (11th month 10.95%).

NUTR. ABS. (b)

Colloidal properties of pupa oil. H. KANEKO and K. YAMAMOTO (Bull. Sericult. Japan, 1934, 6, 4—5).—The relative viscosity (η) of pupa oil is given by $\log \eta = 1.85 - 0.009t$ ($t > 20^\circ$), $\log \eta = 5.30 - 0.166t$ ($t > 6^\circ < 20^\circ$). When mixed with oils of higher η the η -concn. curves are S-shaped, with oils of lower η they are concave. In dispersions in org. solvents $\log \eta \propto$ concn.

A. G.

Saturated fatty acids of Japanese chrysalis oil. S. UENO and H. IKUTA (J. Soc. Chem. Ind. Japan, 1934, 37, 124—126b).—The Me esters of the solid fatty acids when fractionally distilled afford Me palmitate and stearate, and the ester of a C_{20} or C_{22} acid, but no Me isopalmitate (cf. A., 1921, i, 699).

J. L. D.

Insect waxes. VII. Fractionation of schizoneuric acid. F. N. SCHULZ and M. BECKER (Biochem. Z., 1934, 270, 386—388).—The Me esters of the acids from schizoneura wax on fractionation at 0.12 mm. indicated the presence of $\frac{2}{3}$ myristic and $\frac{1}{3}$ palmitic acid (cf. A., 1933, 1066).

P. W. C.

Formation of a fat-soluble red pigment in cured meats. O. NOETZEL and A. PAWLETTA (Pharm. Zentr., 1934, 75, 361—365).—A red pigment (I) appears in the fat (II) of meat after 5 days' curing at room temp. with KNO_3 . (I) is destroyed when (II) is saponified or becomes rancid. The absorption spectrum (III) of (I) in melted (II) is identical with that of oxyhaemoglobin, except that the band in the yellow-green is absent. (I) turns first brown, then yellow, when exposed to air, and then gives the (III) of methaemoglobin. (I) is also formed, although to a smaller extent and more slowly, when meat is cured without KNO_3 .

E. C. S.

Determination of pyruvic acid in muscle. A. HAHN and H. NIEMER (Z. Biol., 1934, 95, 169—172).—The minced muscle is treated with semicarbazide hydrochloride (I); proteins are removed with boiling aq. $(NH_4)_2SO_4$. Excess of (I) is removed with PhCHO, and the $AcCO_2H$ converted into phenylhydrazone, and weighed as such.

H. D.

Use of aqueous extracts for determining glycogen and total carbohydrate in the liver. C. TSAI (Chinese J. Physiol., 1933, 7, 343—352).—After one aq. extraction of rabbit-liver, the glycogen (I) content of the residue is 30—60% > that of the extract, and after several aq. extractions, the residue still contains 0.356 g. of (I) per 100 g. A single boiling- H_2O extraction may not therefore be used for the determination of total carbohydrate or (I).

A. L.

Carbohydrate content of liver and muscle in the wild and domestic duck. S. SUZUKI (Japan. J. Med. Sci. Biochem., 1933, 2, 277—283).—The glycogen and glucose vals. for the wild are similar to those for the domestic duck. In both species breast muscle contains more carbohydrate than leg muscle.

NUTR. ABS. (m)

Localisation of mineral salts in cells of mammalian tissues by micro-incineration. G. H. SCOTT (Amer. J. Anat., 1933, 53, 243—288).—Only Fe and Si can be recognised with certainty. Ca in large, or aggregates of small, cells can be recognised. In dividing cells the mineral matter is conc. in the chromatin. Exposed surfaces such as cell surfaces along vascular channels show concn. of inorg. salts.

CH. ABS.

Relation of specific potential of gastric mucous membrane of warm-blooded animals to hydrochloric acid secretion. H. SARRE (Z. Biol., 1934, 95, 135—145).—A portion of the mucous membrane of a cat's stomach was ligatured to a ring; the membrane potential (I) was determined by a KCl-agar electrode dipping into the trough so formed; $[H^+]$ and $[Cl^-]$ were determined by Sb and AgCl electrodes, respectively. Secretion is accompanied by an increased negativity of (I), independent of its initial val., corresponding with the increased $[H^+]$. The $[Cl^-]$ remains const. during secretion.

H. D.

Composition of pure intestinal juice from the lowest segment of the ileum in man. A. BICKEL and H. R. KANITZ (Biochem. Z., 1934, 270, 378—381).—General chemical analysis of the juice is carried out, and the presence of amylase and erepsin but absence of lipase is detected. The type of nutrition does not affect the enzymic content of the secretion.

P. W. C.

Taurocholic acid. II. T. KAZUNO and K. YAMAZAKI (Z. physiol. Chem., 1934, 224, 160—162).—From the Na salt isolated from dog's bile by Tanaka (A., 1933, 1162) amorphous taurocholic acid (I), m.p. about 125° (decomp.), $[\alpha]_D^{20} + 38.8^\circ$ in EtOH [Na salt, m.p. 180° , $[\alpha]_D^{20} + 23.9^\circ$; cryst. Ba salt (+ $5H_2O$), decomp. $225—227^\circ$, $[\alpha]_D^{20} + 25.6^\circ$ in H_2O], was obtained. (I) was isolated as Na salt from the bile of *Scomberomorus Nipponius*.

J. H. B.

Variations in the solids-not-fat content of milk. I, II. S. BARTLETT (J. Dairy Res., 1934, 5, 113—123).—Little change occurs in the solids-not-fat during an individual milking. Variations over a complete lactation period are recorded, and indicate the influence of age and pregnancy.

A. G. P.

Phosphorus compounds of milk. V. Phosphorus partition in milk with preliminary observations on milk-phosphatase. W. R. GRAHAM, jun., and H. D. KAY. VI. Effect of heat on milk-phosphatase. Simple method for distinguishing raw from pasteurised milk, raw from pasteurised cream, and butter made from raw cream from that made from pasteurised cream. H. D. KAY and W. R. GRAHAM, jun. (J. Dairy Res., 1933, 5, 54—62, 63—74).—V. Methods for determining the P distribution in milk are examined. The acid-sol. ester-P (I) in milk is approx. $\frac{1}{4}—\frac{1}{5}$ of the inorg. P. A phosphatase in milk (optimum pH 9.0) causes fairly rapid changes in the amount of (I) in milk on keeping, and possibly within the mammary gland. Differences in the level of (I) are associated with different breeds of cows.

VI. The phosphatase of milk is sufficiently heat-labile to be destroyed by effective pasteurisation (II).

and its presence or absence serves to indicate (II). A simple technique for performing the test is described.

A. G. P.

Cholesterol content of milk in relation to that of food. H. DAM (*Z. physiol. Chem.*, 1934, 224, 127—128).—Administration of cholesterol (I) to goats for 3 days caused no increase of (I) in the milk.

J. H. B.

Cholesterol content and antirachitic activation of milk constituents. S. ANSBACHER and G. C. SUPPLEE (*J. Biol. Chem.*, 1934, 105, 391—404).—A colorimetric method for determination of cholesterol (I) after pptn. with digitonin is described. (I) in butter-fat (II) varies between 0.24 and 0.34%. In milk 18% of (I) is associated with the proteins (III), of which most is with the lactalbumin in a relatively const. amount. The fat associated with (III) holds more (I) than does (II). (I) associated with (III) contains a substance which can be activated antirachitically.

H. G. R.

Presence of cholesterol in faeces. R. SCHOENHEIMER (*J. Biol. Chem.*, 1934, 105, 355—357).—By bromination in EtOH unsaturated sterols are rendered unprecipitable by digitonin, and can thus be separated from saturated sterols. In this way cholesterol was isolated from human and canine faeces.

C. G. A.

Urine of normal dairy cows. G. F. BODDIE (*Vet. Rec.*, 1933, 13, 1128—1133).—Samples of urine taken during autumn, winter, and spring from apparently healthy cows on good mixed diets contained no albumin, bile-pigment or -salts, blood-pigment, (except in three cases), or blood. Sugar (58% of cases), indican, creatinine (small amounts), glycuronic acid, mucus (25% of cases), urea, and COMe_2 (44% of cases) were present.

NUTR. ABS. (b)

Comparison of urinary total nitrogen for one-day and four-day periods. B. L. KUNERTH (*Trans. Kansas Acad. Sci.*, 1933, 36, 157—158).—A composite sample may be used to calculate daily N excretion.

CH. ABS.

Determination of thiocyanate in urine. E. J. BAUMANN, D. B. SPRINSON, and N. METZGER (*J. Biol. Chem.*, 1934, 105, 269—277).—HCN, formed by the action of CrO_3 on SCN' , is removed by aeration, trapped in NaOH, and titrated with AgNO_3 (cf. A., 1919, ii, 530). If < 5 mg. SCN' per 100 c.c. of urine are present, a preliminary purification is necessary to remove traces of NH_2 -acids and other N compounds (cf. A., 1933, 1188).

A. E. O.

Detection and determination of glycogen in urine. H. CAPPENBERG (*Arch. Pharm.*, 1934, 272, 559—561; cf. A., 1931, 758).—Glycogen (I) occurs most frequently in urine of patients suffering from liver- or bile-infection, gout, or arteriosclerosis, being accompanied in the last two cases by much PO_4''' and $\text{C}_2\text{O}_4''$. Pure (I) gives the same reactions as when obtained from urine, whether or not sugar or ovalbumin is also present. (I) gives the Mayrhofer (Polenske) reaction for intact starch. It can be determined by its slow reduction of Fehling's solution (II); if sugar is also present, the Cu_2O formed thereby is removed, and (I) determined by further oxidation of the filtrate. (I)

can be pptd. by Esbach's reagent and then determined by (II).

R. S. C.

Incidence of sugars in the urine of infants and children. M. FIKRI and M. A. EL-SAYED (*Arch. Dis. Children*, 1933, 8, 409—412).—In 63 healthy children only 1 case, a breast-fed infant, showed a reducing agent, lactose (I), in the urine, and it was present only once. Out of 87 sick children, 11 showed a reducing substance in the urine, which was found to be (I) in 8 cases, and (I) plus glucose in 3 cases. In the (I) cases, the excretion of the sugar was transient in 5, and persistent in 3, these 3 being cases of Pott's disease, multiple boils, and pulmonary tuberculosis.

NUTR. ABS. (b)

Fasting blood-sugar and blood-sugar curves after oral administration of glucose in allergic subjects. J. VAN NIEKERK (*Z. ges. exp. Med.*, 1933, 90, 617—624).—In allergic patients, during a period without an attack, the fasting blood-sugar was normal. After 50 g. of glucose, the fall in blood-sugar to fasting level was usually delayed: occasionally the peak was higher or lower, and the rise slower than normal. The type of curve cannot be used as diagnostic of allergy.

NUTR. ABS. (b)

Nutritional anæmia of the rat. X. Hæmoglobin production and iron and copper metabolism with milk of low copper content. F. C. BRNG, E. M. SAURWEIN, and V. C. MYERS (*J. Biol. Chem.*, 1934, 105, 343—354).—Rats rendered anæmic by a diet of milk containing 0.14 mg. of Cu per litre showed an increase in hæmoglobin content (I) on oral administration of 0.5 mg. of Fe per day. Addition of 0.025 mg. of Cu per day as well restored (I) to the normal level. Intraperitoneal injection of Fe had the same effect, possibly due to increased retention of Cu.

C. G. A.

Specific catalytic action of copper in the oxidation of glutathione. A. QUARTAROLI (*Annali Chim. Appl.*, 1934, 24, 225—226).—Whereas blood contains 1 part of Cu per 300—350 parts of Fe, hæmatin contains, contrary to Voegtlin *et al.* (A., 1931, 763; 1932, 77; this vol., 90), 124 mg. of Cu per kg. (A., 1932, 1182). The necessity of adding small proportions of Cu salts to Fe salts used to combat experimental anæmia is discussed.

T. H. P.

Gastro-intestinal studies. III. Determinations of enzymes on autopsy specimens from cases of pernicious anæmia and pellagra. O. M. HELMER, P. J. FOUTS, and L. G. ZERFAS (*Arch. Int. Med.*, 1934, 53, 675—679).—Gastric mucosa taken *post mortem* from patients with pernicious anæmia contained no pepsin or rennin, whilst in cases of pellagra subnormal quantities were present. Neither disease was associated with decreased proteolytic, amylolytic, or lipolytic activity of the pancreas, whilst the intestinal mucosa was normal in respect of enterokinase action.

W. O. K.

Blood-calcium during consolidation of fractures. J. PERVES (*Compt. rend. Soc. Biol.*, 1933, 114, 526—528).—The blood-Ca rises after bone fracture and returns to normal when consolidation is complete.

NUTR. ABS. (m)

Bones of native horses affected with osteomalacia. M. D. SUMULONG (Philippine J. Sci., 1934, 53, 141—157).—The wt. and ash content of the bones are diminished, the latter from 55.9 to 49.5%. The chief reduction is in CaCO_3 , $\text{Ca}_3(\text{PO}_4)_2$, and Na_2CO_3 .

H. G. R.

Relation between the physical character of food and dental caries in albino rats. C. A. LILLY and L. WILEY (J. Nutrition, 1934, 7, 463—472).—Appearance of caries in rats receiving standard rations containing coarse maize meal is related to the physical condition of the diet rather than to its Ca and P contents. Cooking or fine grinding prevented caries. Vitamin-D was without effect. A. G. P.

Calcium and cholesterol in blood and gall-bladder bile in cholelithiasis and cholecystitis. M. CATTANEO (Z. ges. exp. Med., 1933, 91, 683—688).—The cholesterol (I) concn. in bile (II) from obstructed gall-bladders was > in (II) obtained from a normal biliary tract. A high (I) val. indicates some obstruction, but a low val. does not necessarily signify the presence of gallstones. The serum-Ca is generally normal in cholelithiasis. In cholecystitis without gallstone formation both the (I) and Ca of (II) were increased. In cholecystitis with cholelithiasis no correlation was obtained between the increases of (I) in (II) and blood.

NUTR. ABS. (b)

Protein-bound sugar of blood and insulin. G. CARRIÈRE and P. MARTIN. **Protein-bound sugar and serum-proteins during insulin hypoglycæmia in normal and diabetic subjects.** G. CARRIÈRE, P. MARTIN, and CARBONNEL (Compt. rend. Soc. Biol., 1933, 114, 135—136, 265—266).—Administration of 15—45 units of insulin does not affect the level of the protein-bound sugar of whole blood or serum, nor are the proteins of serum affected.

NUTR. ABS. (m)

Metabolism of carbohydrate and fat and its relation to insulin: effects of high-carbohydrate-low-fat diet in diabetes. E. P. POULTON (Proc. Roy. Soc. Med., 1933, 26, 1591—1607).—Indirect calorimetry, involving calculations based on the Zuntz-Schumberg theory, is liable to serious errors. The heat produced appears to be \propto the CO_2 liberated, whilst under basal conditions there is a const. combustion ratio of carbohydrate and fat. Insulin increases combustion and stimulates conversion of carbohydrate into some less oxygenated substance.

NUTR. ABS. (m)

Variations in blood-potassium and -calcium in acute eczema and dermatitis. G. I. UMANSKY and A. P. STEPANOVA (Wien. klin. Woch., 1933, 46, 1262—1265).—An invariable increase in the blood-K and sometimes a decrease in the blood-Ca occur in dermatitis or acute eczema with œdema (I). The K tends to decrease and the Ca to increase with the disappearance of (I).

NUTR. ABS. (m)

Micro-incineration of the liver in Rift Valley fever. E. S. HORNING and G. M. FINDLAY (J. Roy. Microscop. Soc., 1934, 54, 9—17).—Incineration of the liver 24—30 hr. after infection with the virus of Rift Valley fever shows changes in the localisation of mineral salts. The ash of chromatin, nucleolus, and

inclusion body can be differentiated. The necrosis occurring in malignancy and CCl_4 poisoning is similar, as regards localisation of inorg. constituents of the tissue, to that which follows certain virus infections.

P. G. M.

Serum-proteins and chlorides in hepatic œdema. Biochemical modifications after novasurol and hepatotherapy. M. RAFFAELE (Arch. Farm. sperim., 1934, 57, 219—238).—Hepatic œdema is attended by a fall in serum-protein, inversion of the normal albumin-globulin ratio (I), and a rise in venous and capillary Cl'. Administration of novasurol or hepatotherapy, or both, brings (I) rapidly to the normal val. in both serum and ascites, and increases urinary Cl' excretion.

R. N. C.

Intermediary metabolism of carbohydrates, experimental hepatitis, and protective liver therapy. G. G. D'ANTONA (Riv. Patol. sper., 1933, 11, 354—380).—In rabbits with experimental liver lesions produced by tuberculin, injection of glucose has no protective action nor regenerative effect on the liver, kidneys, and spleen, and is actively harmful, since it increases fatty infiltration and has a deleterious action on the kidneys. The disappearance of the liver-glycogen is the result of the tuberculin poisoning.

NUTR. ABS. (m)

Enzymes in glycogen-storing disease. W. HERTZ (Klin. Woch., 1933, 12, 1725—1727).—The diastase of blood and urine is raised, blood-glycolysis is little affected, and the lipolytic activity of the blood-serum and liver is sometimes increased.

NUTR. ABS. (m)

Metabolism in glycogen-storing disease. W. HERTZ (Z. Kinderheilk., 1933, 55, 588—601).—In a dwarf child of 11 suffering from the disease the N exchange was not raised in spite of a high basal metabolic rate. There was no disturbance of NH_2 -acid metabolism, nor increased urobilin excretion, but the creatine-creatinine output was high. The condition is due, not to disordered liver function, but to exaggerated glycogen-storing power of the liver and other organs.

NUTR. ABS. (m)

Diagnostic significance of sodium chloride metabolism in liver disease. L. RÓSA (Orvosi Hetilap, 1933, 77, 1050—1051).—Normal 24-hr. urine contains < 0.72—0.74% of NaCl. In the absence of acute infections and diabetes a lower concn. is characteristic for liver-disease.

NUTR. ABS. (b)

Origin and significance of tyrosinuria in liver disease. S. S. LICHTMAN (Arch. Int. Med., 1934, 53, 680—688).—Marked tyrosinuria (I) was found in acute yellow atrophy (II), whilst mild and transitory (I) occurred in subacute (II) and certain other diseases of the liver and bile passages. W. O. K.

Creatinine in blood-serum and cerebrospinal fluid. R. B. MAYDELL (Z. ges. exp. Med., 1933, 91, 455—462).—In normal subjects the serum contains 1.6 mg. and the fluid 1.18 mg. of preformed creatinine (I) per 100 c.c. In chronic interstitial nephritis the (I) val. rises more slowly in the fluid than in the serum. Vals. > 4.0 mg. (serum) and 2.4 mg. (fluid) occur when there is tendency to uræmia; vals.

>14 and 5 mg. are obtained only in last stages of chronic nephritis and malignant nephrosclerosis.

NUTR. ABS. (m)

Lipin-protein equilibrium in serum of patients suffering from skin or lipæmic affections. A. SARTORY, R. SARTORY, J. MEYER, and J. CUENI (Compt. rend., 1934, 198, 1724—1726).—Total proteins (I) are unchanged in obesity, although the albumin (II)-globulin (III) ratio depends on the p_H . In hyperkeratosis, (II)/(III) is reversed in val., whilst in fatty dystrophy of the cornea the metabolism of fatty acids and cholesterol is abnormal. J. L. D.

Production of hypochloræmia in the dog with survival. J. BOTTIN (Compt. rend. Soc. Biol., 1933, 114, 1392—1394).—Death, following intestinal obstruction, is not due entirely, if at all, to hypochloræmia (I), since vals. for blood-Cl, approximating to that found in (I), have been obtained experimentally in the dog with survival. NUTR. ABS. (m)

Organo-aciduria in pregnancy and physiological puerperium. F. P. DONEDDU (Arch. Farm. sperim., 1934, 57, 201—218).—The mean daily excretion of org. acids in the urine, equiv. to 330 c.c. of 0.1N, remains const. throughout the pregnancy period, but falls slowly during the first few days of puerperium. R. N. C.

Effect of pregnancy and parturition on some blood and urinary constituents in the ewe. S. W. JOSLAND (New Zealand J. Sci. Tech., 1934, 15, 358—363).—During 2 months prior to and 6 weeks after parturition changes in serum-Ca and -Mg were insignificant, the inorg. P declined somewhat at or near parturition, whole blood-K varied irregularly, and -Na was slightly higher after parturition. Throughout the period the NH_3 - and total N in the urine varied considerably, the total P was approx. const., and protein, sugar, and $COMe_2$ were detectable only occasionally. A. G. P.

Calcium metabolism and chronic rheumatism. F. COSTE, A. GRIGAUT, and P. CHARMANT (Compt. rend. Soc. Biol., 1933, 114, 895—897).—In arthritis deformans (I) the serum-Ca is 9.3—11.9 mg. per 100 c.c. No support is given to the view that parathyroid dysfunction is concerned with (I). NUTR. ABS. (m)

Gastric tetany. R. KLINGNER (Z. ges. exp. Med., 1933, 92, 129—146).—Hypochloræmia occurs with increase of non-protein-N and alkali reserve. Serum-Ca increases. Parenteral administration of H_2O and NaCl leads to large retention of both with disappearance of the severe symptoms and return of blood constituents to normal. NUTR. ABS. (m)

Blood-cholesterol and thyroid disease. III. Myxœdema and hypercholesterolæmia. L. M. HURXTHAL (Arch. Int. Med., 1934, 53, 762—781).—Thyroïdectomy is frequently followed by hypercholesterolæmia (I) with or without myxœdema and a low metabolic rate. In the absence of other causative factors (I) suggests thyroid deficiency. W. O. K.

Inverted sugar tolerance curves in a case of Addison's disease. E. L. TURNER (Endocrinology, 1933, 17, 699—702).—Low blood-sugar (I) vals. in

Addison's disease have been recorded. In the case described, a series of (I) vals. after oral administration of glucose were < the fasting (I) val. (inversion curve). An intravenous glucose-tolerance test indicated that gastro-intestinal absorption was a factor. NUTR. ABS. (b)

Hypoglycæmia due to intravenous insulin in endocrine disturbances. M. LABBÉ, A. ESCALIER, and P. UHRY (Compt. rend. Soc. Biol., 1933, 114, 890—892).—The hypoglycæmic response is normal in scleroderma, acromegaly, and diabetes insipidus (I) treated with pituitary extracts; it is enhanced in Recklinghausen's disease, exophthalmic goitre, and untreated (I). In a case of Addison's disease it was intense. NUTR. ABS. (m)

Effect of toxæmia on tolerance for glucose and on the action of insulin. J. S. SWEENEY, N. BARSHOP, and L. C. LOBELLO (Arch. Int. Med., 1934, 53, 689—698).—The lowered sugar tolerance in rabbits resulting from diphtheria toxin is removed by giving a suitable quantity of insulin a short time before the glucose. W. O. K.

Carbohydrate metabolism in pulmonary tuberculosis. S. SHIMIZU (Tôhoku J. Exp. Med., 1933, 22, 132—148).—The blood-sugar level in pulmonary tuberculosis is not essentially abnormal, but may show wide variations in severe cases. Hyperglycæmia (I) may be due to secondary causes, e.g., loss of blood. Hypoglycæmia occurs only in the final stages of cachexia. Alimentary (I) tends to be prolonged. NUTR. ABS. (b)

Metabolic rhythm, day and night, in the pigeon. E. BURCKARD, L. DONTCHEFF, and C. KAISER (Ann. Physiol. Physico-chim. biol., 1933, 9, 303—368).—The basal metabolic rate (I) in normal pigeons rises by 2.2% for each degree of fall in temp. from 30° to 20°; below 20° the increase is 3.3%. If ruffling of feathers be prevented, heat loss is increased and the increase in (I) is then 3.2% from 30° to 20° and 3.8% from 20° to 5°. The difference between day and night (I) is 15%. NUTR. ABS. (m)

Fertilisation and temperature coefficients of oxygen consumption in eggs of *Arbacia punctulata*. B. B. RUBENSTEIN and R. W. GERARD (J. Gen. Physiol., 1934, 17, 677—685).—In a resting state the temp. coeff. Q_{10} is 4.1, but on fertilisation and on cytolysis this falls to 1.8 and 1.9, respectively. The factor causing increase in O_2 consumption is variable and depends on the temp. and on the species. H. G. R.

Oxidation-reduction processes in muscular work. III. Glutathione. A. CHARIT and N. CHAUSTOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 26—29).—Stimulation of the gastrocnemius (dog) by an induction current for 15—60 min. causes a decrease in the reduced glutathione (I) content of arterial and (more so) venous (femoral) blood, and a corresponding increase in the oxidised glutathione content; a concomitant increase of (I) in the muscle tissue is observed. J. W. B.

Oxidation-reduction processes in muscular work. IV. Ferric and ferrous compounds. A. CHARIT and A. KOSTIN (Compt. rend. Acad. Sci.

U.R.S.S., 1934, 2, 194—197).—During the stimulation of muscle the Fe^{III} content increases by $> 100\%$. Muscle activity is associated with the reaction $\text{Fe}^{\text{II}} \rightleftharpoons \text{Fe}^{\text{III}}$, thus supporting Warburg's theory of the rôle of org. Fe compounds in muscle contraction.

F. O. H.

Chemical changes accompanying muscular activity and hyperthermia. II. Composition of the muscle, liver, and blood of normal dogs.

J. HOUGET (Ann. Physiol. Physico-chim. biol., 1933, 9, 245—302).—Dogs kept for several weeks on identical diets do not show the same reserves in muscle, liver, or blood. H_2O , lipin, acid-sol. and total P show only slight, but other constituents may show large, individual variations. The composition is always characteristic for each tissue.

NUTR. ABS. (m)

Glycogen metabolism of muscle and neural influence thereon. I. Glycogen formation in denervated muscle. J. BAUM and E. PICHLER. **II. Glycogenolytical reflex.** J. BAUM, W. CHRISTEN, and E. PICHLER (Pflüger's Archiv, 1933, 233, 35—42, 43—50; Chem. Zentr., 1933, ii, 2850).—I. In winter the glycogen content (I) of a denervated frog-extremity is approx. 25% $>$ that of the normal portion. In summer a similar effect is obtained only by the simultaneous addition of insulin and glucose. After extirpation of the pancreas the increase is only 8% in denervated muscle and 16% in the dehepatised animal. The increase in (I) can be detected 4 hr. after the operation and reaches a max. in 24 hr.

II. After the removal of one gastrocnemius (I) the glycogen content of the other falls approx. 20%; this fall persists after sympathectomy (II). The glycogenolytical action of the sympathetic is directed straight to the muscle. The glycogenolytical reflex should occur more in the spinal nerves. Extirpation of (I) and (II) lead to a decrease in creatinephosphoric acid in the (I) of the other side.

L. S. T.

Glycogen metabolism of muscle and neural influence thereon. III. Proprioceptive glycogenolytical reflex. O. LOEWI and E. PICHLER (Pflüger's Archiv, 1933, 233, 51—56; Chem. Zentr., 1933, ii, 2850—2851).—The influence of strychnine convulsions on glycogenolysis is examined.

A. A. E.

Rôle of the adrenals in the resynthesis of muscle-glycogen after fatigue. R. G. DAMBROSI, F. L. LOEYR, and A. NOVELLI. **Rôle of the liver and pancreas in this resynthesis. Effect of section of the vagi or splanchnic nerves on this resynthesis in the dog. Rôle of the pancreas and the vagi in this resynthesis after fatigue in the cat.** R. G. DAMBROSI (Compt. rend. Soc. Biol., 1933, 114, 1219—1221, 1222—1224, 1224—1226, 1228—1230, 1230—1232).—In adrenalectomised dogs, the rate (I) of resynthesis of muscle-glycogen after fatigue is retarded. (I) is not increased by injection of glucose, but is made normal or above normal by injection of an extract of the adrenal cortex. In hepatectomised dogs, (I) varies with the level of the blood-sugar. Intravenous injection of glucose causes rapid resynthesis. In pancreatectomised dogs, (I) is little affected for a few hr. after the operation, but later is greatly retarded. Neither etherisation nor incomplete

pancreatectomy has this effect, which is also avoided after complete pancreatectomy by injection of insulin or grafting of pancreas in the neck. Resynthesis of muscle-glycogen after fatigue is unaffected in the dog by section of the vagi or of the splanchnics or of both together. In pancreatectomised cats (I) is retarded. Under chloralose, bilateral vagotomy does not cause diminution in (I), but Et_2O anaesthesia or respiratory troubles do so.

NUTR. ABS. (m)

Passage of glycogen through the hæmochorial placenta. B. SZENDI (Z. Anat. Entw., 1933, 101, 791—798).—Glycogen (I) is supplied to the (rat) foetus not direct from the maternal blood-stream, but from the decidua where it is synthesised. The maternal placenta contains (I) cells (II) which make the (I) from the maternal blood-sugar. (II) pass over into the villi by means of the lymphatics as whole cells, after which (I) passes to the foetal blood.

NUTR. ABS. (m)

Blood-sugar equilibrium and gastric secretion. BAISSSET and BUGNARD. **Blood-sugar equilibrium and intestinal secretion.** A. BAISSSET. **Blood-sugar equilibrium in the depancreatized dog and in the normal dog following feeding.** BAISSSET, BUGNARD, and ROUZAUD. **Blood-sugar equilibrium following injection of glucose.** **Blood-sugar equilibrium and retention of sugar in tissues.** BASTIEN, BOUISSET, BUGNARD, and ROUZAUD. **Injection of glucose and retention in the liver.** BASTIEN, BOUISSET, and BUGNARD (Le Sang, 1933, 7, 875—881, 882—893, 894—901, 902—907, 908—913, 914—920, 921—932).—In dogs with cesophageal and gastric fistulae sham-fed with minced meat, blood-sugar rises with onset of gastric secretion (I) and attains a max. 1 hr. after the meal. The rise continues after the (I), returning to normal in about 3 hr. and is followed by hypoglycæmia (II). Where no (I) occurs (dogs drinking but refusing to eat) blood-sugar does not change. (I) and hyperglycæmia (III) are accompanied by a rise in blood- p_{H} and alkali reserve. In Pavlov pouch dogs (I) stimulates duodenal secretion with little change in blood-sugar (5 mg. per 100 c.c.). In gastrectomised dogs ingestion of HCl induces intestinal secretion and reduces blood-sugar. Injection of HCl into the duodenum in normal dogs also causes (II) of degree varying with the individual. A meal of potatoes causes (III) in dogs, varying from 15 to 80 mg. per 100 c.c., or may cause (II). A meal of meat causes little change, and of meat and potatoes together a variable (III). The largest increases in blood-sugar follow a meal of bread and milk. Alimentary (III) in depancreatized dogs following a meal of meat is much $>$ in normal dogs, but rapidly diminishes as in them. A regulatory mechanism, independent of the pancreas, is suggested, since blood-sugar equilibrium is re-established after pancreatectomy. Daily intravenous injection into unanaesthetized dogs of glucose in increasing amounts causes a rise in blood-sugar approx. \propto the amount injected, and a return to normal after an interval which also increases with the dose. The max. increase in blood-sugar is attained before completion of injection and is followed by a rapid fall with return to normal in 1.5 hr. After injection of glucose (1 g. per kg.) the

rise in blood-sugar is greater in arterial than in venous blood at first, indicating retention in the tissues, but after about 45 min., venous blood-sugar is = or > arterial. In anaesthetised dogs exclusion of the liver by portal jugular anastomosis causes a variable (II), arterial blood-sugar falling more rapidly than venous with inversion after about 45 min. Following injection of 0.75 g. glucose per kg., the sugar rapidly disappears from the blood and there is again inversion of arterial and venous vals. The glucose stored following injection is more rapidly utilised by the normal than by the dog with exclusion of the liver, but in both cases blood-sugar returns to normal or below normal. Storage following injection is therefore independent of glycogen storage, although the utilisation of stored glucose is disturbed in absence of the liver.

NUTR. ABS. (m)

Assimilation of sugar in Eck fistula dogs. Blood-sugar after intravenous administration of sugar. S. LIVIERATO, M. VAGLIANO, and A. DERVENAGA (Compt. rend. Soc. Biol., 1933, 114, 462—464).—The glycaemic response of an Eck fistula dog to an intravenous injection of lactose or fructose is similar to that of a normal dog, but injection of glucose results in a hyperglycaemia > that found in the normal dog.

NUTR. ABS. (m)

Blood-sugar regulation after intravenous administration of large doses of glucose. M. FENICIA (Riv. Patol. sper., 1933, 11, 225—240).—After intravenous injection of massive doses of glucose into fasting dogs, the resultant hyperglycaemia rapidly disappears, due to an emergency fixation of the sugar by the tissues. Later, this sugar is discharged into the circulation, from which it is probably taken up by the liver.

NUTR. ABS. (b)

Carbohydrate metabolism. I. In the new-born. E. W. WINTER (Arch. Gynäkol., 1933, 154, 354—373).—The mature new-born infant (I) has a physiological hypoglycaemia. The tolerance (II) of (I) to a single dose of glucose is normal, but a second dose, given about 90 min. after the first, results in a greater hyperglycaemia. This impairment of carbohydrate (II) during the early post-natal period may be due to a certain "unreadiness" of the infantile carbohydrate-regulating mechanism.

NUTR. ABS. (b)

Sugar metabolism in old age. Alimentary hyperglycaemia. J. NITZULESCU, I. ORNSTEIN, and M. SIBI (Compt. rend. Soc. Biol., 1933, 114, 1136—1138).—Determinations were made of blood-sugar (I) in fasting (aged) subjects after ingestion of 50 g. of glucose. Average vals. over a period of 3 hr. for each decade from 50 to 90 years are given. There was no progressive deviation of the (I) curve with increasing age, nor was glycosuria regularly found.

NUTR. ABS. (b)

Biological availability of soya-bean carbohydrate. W. H. ADOLPH and H. C. KAO (J. Nutrition, 1934, 7, 395—406).—Approx. 40% of the carbohydrate is utilisable by rats.

A. G. P.

dl-Lactic acid as nutriment. I. Assimilation and toxicity in the rabbit. J. A. COLLAZO, J. PUYAL, and I. TORRES (Anal. Fis. Quim., 1933, 31, 672—684).—The metabolism of lactic acid is discussed.

Rabbits tolerate oral doses of 5—6 g. of Na lactate per kg. with slight dyspnoea. After administration the blood-lactic acid rises to 200—250 mg. per 100 c.c. and the blood-sugar increases simultaneously by as much as 50% of the initial val.

R. K. C.

Stimulating action of diet on production of glycogen from lactic acid in the liver. O. M. DOMANTOVITSCH (Problems of Nutrition, 1933, 2, 25—32).—In rats given special diets, followed, after an 18-hr. fast, by 0.2 g. of Na lactate (85% of which is absorbed), glycogen production (I) in the liver when meat is the chief food is > when it is wheat-protein or caseinogen. (I) is also stimulated by meat extract, lecithin, and PO_4''' .

NUTR. ABS. (m)

Production of liver-glycogen in the cat, under various conditions, following infusion of ammonium lactate. R. GRANT (J. Physiol., 1933, 80, 41—47).—Production of liver-glycogen (I) from NH_4 lactate occurs in the chloralosed cat with all organs intact, but is diminished or absent after splenectomy (II). After (II) infusion of acetylcholine with or after the lactate leads to an increase of (I) of the same order as that found in intact cats.

NUTR. ABS. (m)

Blood-lactic acid in man during rest. L. C. COOK and R. H. HURST (J. Physiol., 1933, 79, 443—454).—There are wide variations (I) in the same individual at different times under apparently identical conditions of bodily rest (II). During (II) the muscles supply no lactic acid (III) to the blood; activity of the sympathetic nervous system with consequent secretion of adrenaline is an unlikely source; the blood receives no demonstrable amount of (III) from the brain; glycolysis is the most probable source of the blood-(III) at rest. (I) during (II) are due to stimulation or depression of glycolytic activity.

NUTR. ABS. (m)

Glycolytic production of blood-lactate. C. L. EVANS, F. Y. HSU, and T. KOSAKA (J. Physiol., 1933, 80, 19—20p).—The rate of lactate formation in defibrinated blood perfused through ventilated lungs indicates that glycolysis is then 2 or 3 times as rapid as when blood is oxygenated by circulation *in vitro*. In the lung about 80% of the glucose lost is converted into lactic acid; in the oxygenator the conversion, which may be associated with hæmolysis, is rather irregular.

NUTR. ABS. (m)

Ketosis in the phloridzinised rat. W. GOLDFARB, S. B. BARKER, and H. E. HIMWICH (J. Biol. Chem., 1934, 105, 283—286).—Unavoidable errors in the determination of the R.Q. made it impossible to conclude that the theoretical ketogenic-antiketogenic ratio of exactly 2 : 1 obtains in phloridzinised rats. The oxidation of keto-acids probably requires the simultaneous oxidation of antiketogenic substances.

A. E. O.

Ketosis in fasted and fat-fed rats. W. GOLDFARB, S. B. BARKER, and H. E. HIMWICH (J. Biol. Chem., 1934, 105, 287—290).—The rats excreted almost no ketonic substances (I) in a large majority of experiments. The non-protein R.Q. indicated that a mixture of fat and small amounts of preformed carbohydrate (II) was oxidised. Assuming a ketogenic-antiketogenic ratio of 2 : 1, and allowing for the (II)

oxidation and errors of method, the calc. and observed yields of (I) were in fair agreement. A. E. O.

Fasting ketosis of monkeys. I. T. E. FRIEDEMANN (J. Biol. Chem., 1934, 105, 335—341).—Fasting monkeys develop ketosis under conditions of metabolism similar to those producing ketosis in man.

C. G. A.

Chemical course of and physiological conditions for formation of ketonic substances from pyruvic acid. E. ANNAU (Z. physiol. Chem., 1934, 224, 141—149).—In the formation of COMe_2 from AcCO_2H in presence of H_2O_2 , 2 mols. of AcCO_2H probably condense to form parapyrvic acid, which, by decarboxylation and oxidation, then yields COMe_2 . The production of COMe_2 is increased by NH_3 and even by NH_4Cl . Oxidation in presence of liver-pulp shows the same effect. NH_3 probably also stimulates AcCO_2H formation in the liver, but has no action on fatty acid ketogenesis. In fasting the liver shows at first increased, later diminished, production of ketones, probably owing to more efficient breakdown of $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$ in prolonged hunger. The factors influencing ketogenesis are glycogen content and increased concn. of free NH_3 . Only the latter favours AcCO_2H production. J. H. B.

Metabolism of neutral fat in central nervous system during embryonic development. A. HADJIOLOV and G. OUZOUNOV (Compt. rend. Soc. Biol., 1933, 114, 578—580).—Neutral fat, although not detectable histologically in the nervous system of adult fowls, can be detected therein during embryonic development. NUTR. ABS. (m)

Influence of rations rich in phosphatides on the animal organism. A. TRAUTMANN (Z. Zucht., 1932, B, 24, 1—164; Bied. Zentr., 1934, A, 4, 339—340).—Soya-bean lecithin (I) was almost completely resorbed by rabbits, dogs, and pigs. The effects on the animals varied with their age and condition. Prolonged administration of small amounts of (I) to the very young favourably influenced live-wt. increases, but larger amounts retarded growth without notable ill-effects on general health. Long hair growth was induced in young pigs. A. G. P.

Transformation of chlorophyll in the animal body. L. MARCHLEWSKI and W. URBAŃCZYK (Bull. Acad. Polonaise, 1933, A, 540—546).—The colouring matter from the air-dried excrement of silkworm larvæ is shown, spectroscopically, to contain anhydro- β -phyllotaonin (I), $\text{C}_{34}\text{H}_{34}\text{O}_5\text{N}_4$ (A., 1912, i, 641), max. absorption at 415.0 μ , identical with Conant's phæopurpurin 18 (A., 1930, 1299). A possible structure for (I) is suggested. J. W. B.

Histolytic properties of regenerating tissue. V. N. ORECHOVITSCH and N. V. BROMLEI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 249—253).—Increases of approx. 100% in the residual N and $\text{NH}_2\text{-N}$ contents indicate that the regenerating tissue formed after amputation of a limb or tail of the axolotl or tadpole is the site of an increased protein degradation. F. O. H.

Protein requirement in man. B. SÜSSKIND (Z. Ver. deut. Zucker-Ind., 1934, 84, 341—356).—The presence of 1 g. of protein (I) per kg. of body-wt. in the

diet is not sufficient for the maintenance of normal condition, even when 70% of the (I) is of high biological val. Lack of (I) cannot be compensated by increasing the fat and carbohydrate contents of the diet.

P. G. M.

Synthesis and degradation of proteins in the laboratory and in metabolism. M. BERGMANN (Science, 1934, 79, 439—445).—A lecture. L. S. T.

Effect of heat on the biological value of meat protein. A. F. MORGAN and G. E. KERN (J. Nutrition, 1934, 7, 367—379).—Cooking of beef muscle or of horseflesh under atm. or increased pressure lowered the biological val. of the protein for maintenance of rats, the effect being rather more marked in the case of beef. A. G. P.

Animal calorimetry. IX. Specific dynamic action of protein. X. Specific dynamic action of fat. Z. ASZÓDI and J. PÉLYI (Biochem. Z., 1934, 270, 389—418, 419—443).—IX. The sp. dynamic action (I) of protein (II) is dependent on the amount of (II) fed, due to its non-deposition and consequent immediate combustion. The amount of heat radiation by the organism is not in direct relationship with the O_2 utilisation after feeding (II).

X. No quant. relationship could be obtained between the (I) and the amount of fat ingested, due to its partial deposition. The amount of heat radiated, as before, does not synchronise with the O_2 utilisation.

P. W. C.

Specific dynamic action of the amino-acids, alanine and glycine. C. M. WILHELMJ (J. Nutrition, 1934, 7, 431—444).—When injected subcutaneously or intravenously into dogs alanine and glycine showed the same sp. dynamic action expressed as g.-cal. per millimol. of NH_2 -acid deaminised (0.2).

A. G. P.

Formation of ammonia from amino-acids in dog's liver *in vivo*. M. POLONOVSKI, P. BOULANGER, and G. BIZARD (Compt. rend., 1934, 198, 1815—1817).—Injection of glycine (I) or *dl*- $\text{NH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ (II) into the blood-stream of a dog causes immediate (2 min.) increase in the NH_3 in the renal vein (smaller increase in the artery), the effect of (II) being > that of (I) and much > that of natural *d*-(II). Hence natural NH_2 -acids, and especially their optical antipodes, are a source of urinary NH_3 . Injection of urea is without effect. J. W. B.

Possible explanation of the function of glutathione in developmental growth. F. S. HAMMETT (Science, 1934, 79, 457).—Through cysteine glutathione accelerates cell proliferation, through glycine it accelerates protein reconstitution, and through glutamic acid it accelerates differentiation and consequent organisation. L. S. T.

Effect of nutritional hypoproteinæmia on the electrolytic pattern and calcium concentration of serum. D. C. DARROW and M. K. CARY (J. Biol. Chem., 1934, 105, 327—334).—In dogs on protein-deficient diet there is no connexion between the serum-protein (I) and $-\text{Cl}'$, $-\text{HCO}_3'$, $-\text{K}$, or $-\text{Na}$, but (I) and serum-Ca are related by $\text{Ca} = 0.47 \times \text{protein} + 2.89$, Ca being expressed in milli-equiv. per litre and protein as %. C. G. A.

Metabolism during growth. Variations with season and age. G. POPOVICIU, G. BENETATO, N. MUNTEANU, and M. SORESCU (Compt. rend. Soc. Biol., 1933, 114, 332—334).—In infants (up to 15 months) and adolescents (18—21 years) blood-lactic acid, -P, and to a certain extent -Ca, -K, and $-p_H$ decrease in Feb. and March, increase in Apr., and fall again in May. Glucose and total CO_2 increase in Feb. and March and decrease in Apr. Lactic acid decreases, whilst glucose increases with age.

NUTR. ABS. (m)

Mineral balance of the diet and its effect on chemical composition of the rat. L. EMERIQUE (Ann. Physiol. Physico-chim. biol., 1933, 9, 765—769).—When the Ca and K contents of a diet containing adequate amounts of vitamin or deficient in vitamin-A are varied the total Ca and K contents of rats are unaltered, but various ratios are changed.

NUTR. ABS. (m)

Comparative calcium and phosphorus retention of pigs on rations supplemented with limestone, bone meal, and "dicapho." J. M. RAMSBOTTOM (Iowa State Coll. J. Sci., 1933, 8, 221—223).—Pigs receiving rations which were adequate except for deficiencies in Ca and vitamin-D were given $CaCO_3$, steamed bone meal, and commercial $CaHPO_4$. No differences in retention of Ca and P were noted except when enough $CaCO_3$ was given to produce Ca : P = 2.13 : 1.

CH. ABS.

Calanus finmarchicus. IV. A. P. ORR. Seasonal changes in weight and chemical composition. V. S. M. MARSHALL, A. G. NICHOLLS, and A. P. ORR (J. Marine Biol. Assoc., 1934, 19, 613—627, 793—827).—IV. Seasonal fluctuations in wt. are recorded for Loch Fyne. Ash content 3.6%, chitin 3%. Fat and protein vary with dry wt.

V. Records from Loch Striven confirm the existence of three main breeding periods. The success of a brood depends on the presence of diatoms during the early stages.

L. D. G.

Consumption of calcium by plankton. L. H. N. COOPER (J. Marine Biol. Assoc., 1934, 19, 747—759).—The English Channel shows in summer a small difference in sp. alkalinity (excess base/chlorinity) between surface and bottom H_2O . This is attributed to removal of Ca from surface layers by plankton.

L. D. G.

Phosphorus and nitrogen in plankton. L. H. N. COOPER (J. Marine Biol. Assoc., 1934, 19, 755—759).—P is determined colorimetrically after digestion with H_2SO_4 and H_2O_2 , and N by a micro-Kjeldahl method.

L. D. G.

Fluctuations in the composition and structure of bone and their bearing on endochondral ossification. S. E. POND (Anat. Rec., 1933, 57, No. 4, Suppl., 64).—During growth, changes in the org. do not parallel changes in the inorg. constituents. The latter are affected by alterations in the circulatory fluids.

NUTR. ABS. (m)

Potassium equilibrium in muscle. W. O. FENN and D. M. COBB (J. Gen. Physiol., 1934, 17, 629—656).—The p_H of the inside of isolated muscle (I) is approx. that of the outside when first dissected,

but tends to follow the p_H of the surrounding medium (II). At each p_H there is a definite $[K']$ in (II) which is in diffusion equilibrium with $[K']$ in (I); this val. is least in the alkaline range so that $[OH'] \times [K']$ is const. The change in p_H in (I) is not equiv. to the diffusion of K' , which is not the only penetrating ion. The irritability of (I) is max. at a concn. of 0.02% of K and probably depends on the ratio of $[K']$ outside to that inside. Swelling of (I) occurs when injury allows both anions and cations to enter, without permitting protein anions to escape. An increase in CO_2 tension causes an increase in acidity in (II) > in (I) and leads to a loss in K' .

H. G. R.

Sodium in metabolism of rats. P. SCHOORL (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 239—245).—Diets low in Na cause poor growth (I) and uræmia. For young rats 0.2% of NaCl in the ration gives good (I). Fertility is not affected by lack of Na, but milk secretion is inhibited.

H. G. R.

Blood-chlorine on mixed diet and during fasting in the dog. Relation to corpuscle and plasma volume. J. BOTTIN (Compt. rend. Soc. Biol., 1933, 114, 1389—1391).—The blood-Cl of a dog fed on a mixed diet (bread, meat, potatoes, and NaCl) was remarkably const. from day to day. During a three weeks' fast, however, the val. fell proportionally to the fall in plasma vol., a rapid return to normal occurring with renewed feeding.

NUTR. ABS. (m)

Diffusion of carbon dioxide in tissues. C. I. WRIGHT (J. Gen. Physiol., 1934, 17, 657—676).—Methods are described for measuring the rate of diffusion of CO_2 in tissue-membranes, tissue-thickness, and the absorption coeff. of CO_2 in tissues; in all cases absorption was slower than in H_2O . The time of saturation with CO_2 is less in non-acidified tissues and the rate depends on CO_2 tension. In a steady state HCO_3' has little effect on diffusion of CO_2 .

H. G. R.

Influence of various constituents of the diet on the ethyl alcohol content of the blood. E. M. P. WIDMARK (Biochem. Z., 1934, 270, 297—308).—When EtOH is administered together with food, a lower blood-EtOH concn. is obtained than when it is taken fasting. A systematic investigation with numerous foodstuffs shows that proteins and NH_2 -acids have a considerable and regular effect in decreasing absorption of EtOH, citric, malic, tartaric, phosphoric, and the higher fatty acids have an effect, but not so regular, whilst H_2O , fat, and carbohydrate are inactive.

P. W. C.

cycloPropane anaesthesia : gas concentrations, respiratory and electrocardiographic changes. M. H. SEEVERS, W. J. MEEK, E. A. ROVENSTINE, and J. A. STILES (J. Pharm. Exp. Ther., 1934, 51, 1—17).—As regards induction of, maintenance of and recovery from anaesthesia, cyclopropane is intermediate in effect between C_2H_4 and Et_2O , and in high concn. is sufficiently toxic to produce cardiac paralysis even under artificial respiration in presence of an adequate alveolar O_2 tension.

A. E. O.

Hyperazotæmia with chloropenia and reduction of alkali reserve. M. CHATRON (Bull. Soc.

Chim. biol., 1934, 16, 405—413).—Administration of NaHCO_3 and NaCl , given in consequence of the chemical findings in the blood and urine, caused much improvement in the condition of a patient who had been poisoned by inhalation of CCl_4 .

W. O. K.

[Pharmacology of] phenanthrene derivatives. II. Effect of protecting the hydroxy-group of 2- and 3-hydroxyphenanthrene. N. B. EDDY (J. Pharm. Exp. Ther., 1934, 51, 75—84).—Conversion of OH into OMe, OEt, or OAc in hydroxyphenanthrenes results in a uniform decrease in activity, which is most pronounced with respect to the analgesic and general depressant actions of 3-hydroxyphenanthrene.

A. E. O.

Mode of action of anthraquinone purgatives in the cat. F. C. MACINTOSH (Proc. Nova Scotian Inst. Sci., 1931—1932, 18, 53—67).—Aloin has no effect on the motility of the small intestine. The higher p_n of the contents of the colon explains the action of anthraquinone purgatives, which normally affect only the large intestine. The purgative action is due to increased peristalsis and, in smaller degree, to inhibition of absorption. Aloin acts on cats only when protein is fed.

P. G. M.

Action of diuretics on the gastro-intestinal canal. A. EBEL and H. MAUTNER (Arch. exp. Path. Pharm., 1934, 175, 128—145).—Subcutaneous injection of diuretics [caffeine, theophylline, novasurol (I)] into rats produces an increased secretion of gastric juice (II) with a high $[\text{Cl}^-]$. This action is inhibited by injection of chloretone, luminal, and, to a smaller extent, urethane and chloral hydrate, but not by veronal or somnifen. With (I) in dogs, removal of (II) through a gastric fistula inhibits the diuresis to an extent indicating that not only the loss of H_2O , but also that of Cl^- and acid, must be concerned in the inhibition.

F. O. H.

Diuresis in the mouse. II. M. R. BONSMANN. III. Quantitative study of the action of anti-diuretics. E. KLEMT (Arch. exp. Path. Pharm., 1934, 175, 322—327, 328—334).—II. Groups of mice are used for the investigation of diuretic action. Theophylline (I), strophanthin (II), and urea (III) produce a two- to four-fold increase in the vol. of urine within 4 hr. of administration. With (I) and (III), the diuretic dose is 14% and with (II) 50% of the min. lethal dose (IV).

III. The (IV) of urethane (V), codeine (VI), and chloral hydrate (VII) to mice is, respectively, 2.30, 0.25, and 0.75 g. per kg. body-wt. With a substance claimed to have a sp. anti-diuretic action, a dose of \times 5% of (IV) should reduce the vol. of urine by \leq 50%. Such a reduction requires 20% of (IV) of (VI) and (VII), whilst even 50% of that of (V) has no inhibitory action; tonephin and morphine are satisfactory, requiring, respectively, 0.03 and 2% of (IV). Interperitoneally injected 0.2% aq. NaCl in mice is absorbed within 1 hr.

F. O. H.

Diuresis. II. Evaluation of diuretic and anti-diuretic substances. W. BENTZ, H. MARX, and K. SCHNEIDER. III. Effect of diathermy of the pituitary region on the water threshold.

W. BENTZ and H. MARX (Arch. exp. Path. Pharm., 1934, 175, 165—168, 169—175).—II. The application of the method previously described (this vol., 216) is given.

III. Diathermic irradiation of the pituitary region of the brain of men and dogs produces a marked anti-diuretic action.

F. O. H.

Dependence of *Digitalis* action on its rate of combination with the heart. Distribution in non-cardiac tissues with various methods of injection. M. HAFERKORN and L. LENDLE (Arch. exp. Path. Pharm., 1934, 175, 248—264).—That the rapid disappearance of *Digitalis* glucosides (I) from the blood (II) is due to a combination with extra-cardiac tissue could not be confirmed (cf. A., 1928, 1400). No marked difference exists between the min. lethal dose to cats when (I) is administered intravenously or arterially, by single or continuous dosage. For some min. after injection (I) are still present in (II); bleeding alleviates the toxic symptoms and yields (II) having an action on a heart-lung prep. typical of (I).

F. O. H.

[Physiological] action of thevetin, a cardiac glucoside of *Thevetia nerifolia*. K. K. CHEN and A. L. CHEN (J. Pharm. Exp. Ther., 1934, 51, 23—34).—Thevetin (I), the sole active constituent of be-still nuts (II), has a digitalis-like action on amphibian and mammalian hearts, its toxicity and potency each being $\frac{1}{2}$ — $\frac{1}{3}$ that of ouabain. (II) kernels contain 3.6—4% of (I) as shown by physiological assay.

A. E. O.

Products of degradation of camphor, camphorquinone, and *epicamphor* in the animal organism.—See this vol., 658, 659.

"Vitacamphor." Pharmacological action of "vitacamphor," and the rôle played by its constituents, π - and p -oxycamphors. K. TAMURA, G. KIHARA, and M. ISHIDATE (Proc. Imp. Acad. Tokyo, 1934, 10, 161—164).—The cardiostimulant action of π -oxycamphor (I) is $>$ of p -oxycamphor (II). The min. effective dose is $>$ that of vitacamphor (III), but $>$ corresponds with the amount of (I) in (III). The autoxidation of (I) is inhibited by (II), and the greater activity of (III) is considered to be due to the presence of both (I) and (II).

A. A. L.

Chronaxie and the action of local anæsthetics on sensory nerves. W. LAUBENDER and C. RAUFENBARTH (Arch. exp. Path. Pharm., 1934, 175, 113—127).—The changes in the chronaxie (I) and rheobase (II) of sensory nerve-fibres (indicated by the crossed extensor-reflex in the spinal frog) due to the anæsthetic action of cocaine, novocaine, percaine, and pantocaine do not serve as a basis for a quant. method of determining their relative efficacy, yet indicate a certain differentiation in their action on (I) and (II).

F. O. H.

Influence of substitution in the benzene ring on the action of surface anæsthetics. F. BOEDECKER and H. LUDWIG (Arch. exp. Path. Pharm., 1934, 175, 307—312).—The effect of introducing various side-chains into the C_6H_6 ring of the compound $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NET}_2\cdot\text{HCl}$ on the anæsthetic action (I) on the rabbit's cornea was investigated. (I) is increased (up to $\times 100$) by alkyl in the o - or

p-position, the effect being proportional to the length of the chain. With unsaturated groups (which react differently from saturated), the position of the double linking is immaterial. Two allyl or propenyl groups have the same influence as one hexyl. MeO and BuO tend, respectively, to weaken and increase (I). Many *p*-derivatives have an inflammatory action which is independent of (I) and increases with saturation of the chain introduced; such compounds have a marked surface activity. F. O. H.

Action of aspirin and calcium-aspirin on growing bone. N. MUTCH (J. Pharm. Exp. Ther., 1934, 51, 112—126).—Relatively large doses of aspirin (I) given daily for a month to young rats did not cause any decalcification of the bone as judged by X-ray translucency. The observed broadening of the calcified zone in ossifying cartilage is due to the (I) mol. as a whole rather than to its acidic nature. Ca-aspirin (approx. composition, $[C_6H_4(OAc)CO_2]_2Ca \cdot 4H_2O \cdot \frac{1}{3}CaCl_2$, prepared by pptn. from a conc. aq. solution of $CaCl_2$, and quite stable when dry) contains absorbable Ca, and has a much less harmful action than (I) on growing bone. A. E. O.

Fixation of phenols by the tissues. A. D. MARENZI (Compt. rend. Soc. Biol., 1933, 114, 802—803).—The average total phenol content of rat tissues, determined by a modification of the method of Theis and Benedict, is as follows: liver 15.8, spleen 21.2, kidney 15.3, heart 12.4, lung 16.2, muscle 19.1 mg. per 100 g. and blood 1.8 mg. per 100 c.c. After injection of 2.5 mg. of phenol per kg., the blood content increases to 2.4 mg. in 5 min. and returns to basal level in 120 min., whilst the kidney content reaches a max. of 16.8 mg. in 60 min. Increase of conjugated phenols persists longer in the kidney, suggesting that they are fixed there. NUTR. ABS. (m)

Chemical constitution, pharmacological action, and enzymic activity. F. PIRRONE (Annali Chim. Appl., 1934, 24, 128—139).—Experiments with adrenaline, ephedrine, ephetonine (*r*-ephedrine), tetrahydro- α -, and β -naphthylamine show that increase in the intensity of the pharmacological action is accompanied by increase in the inhibiting effect on the velocity of alcoholic fermentation. T. H. P.

Hyperglycæmic action of amines. R. C. ANDERSON and K. K. CHEN (J. Amer. Pharm. Assoc., 1934, 23, 290—295).—With amines of the types $Ph \cdot CH_2 \cdot NHR'$, $OH \cdot CHPh \cdot CHR \cdot NR'R''$ (I), and (I) with OH and OAlk substituents *m* and *p* to the side-chain (some 40 studied in all), the hyperglycæmic action increases with the no. of C atoms in R, R', and R''. Only adrenaline and closely related compounds are active in very small doses, and raise the blood-sugar by subcutaneous injection. In general, there is little correlation between pressor and hyperglycæmic actions. A. E. O.

Increase of the toxicity of quinine on ultra-violet irradiation. V. V. ALPATOV and O. K. NASTIUKOVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 238—243).—Ultra-violet irradiation increases the toxicity of aq. quinine hydrochloride to *Paramecium caudatum*. F. O. H.

[Pharmacological action of] morphine, codeine, and derivatives. IV. **Hydrogenated codeine isomerides.** N. B. EDDY and (in part) L. F. SMALL (J. Pharm. Exp. Ther., 1934, 51, 35—44; cf. A., 1932, 965).—Saturation of the double linking in ring III of codeine (I) and its isomerides causes a decrease in toxicity, in the augmenting effect on reflexes, and in convulsant action, but an increase in analgesic and respiratory effects. The order of effectiveness of the hydrogenated compounds (II) is not the same as that of (I) and its isomerides. Practically, dihydroisocodeine seems to be more important than the other (II); it is less toxic than (I), and its activity, especially in the production of analgesia, is much greater. A. E. O.

Physiological action of sarothamnine and genisteine. R. HAZARD (Compt. rend., 1934, 198, 1945—1947).—Sarothamnine (I), when injected into dogs, has a depressor action. It augments the vasoconstrictor (II) and hypertensor (III) effects of adrenaline (IV) by paralysis of the vagus, whilst suppressing the reflex bradycardia. Genisteine (V) has no depressor action, it increases (II) and (III) effects of (IV), but suppresses the vagal reflex effect. (I) and (V) suppress the action of acetylcholine and nicotine on the cardiac vagus. R. S. C.

Plant cholagogues. L. SCHINDEL (Arch. exp. Path. Pharm., 1934, 175, 313—321).—Addition of onions to the diet of dogs increases the amount and bile acid content of the bile. Fractionation of extracts yields an active concentrate sol. in H_2O and EtOH. A similar principle occurs in artichokes, but not in radishes. F. O. H.

Effect on blood-sugar of ligature of the portal vein and its branches in the dog. N. FLESSINGER and R. CATTAN (Compt. rend. Soc. Biol., 1933, 114, 483—486).—A deficiency of pancreatic and splenic hormones, general anæmia, and especially congestion of the abdominal veins are responsible for the sudden hyperglycæmia produced by this operation. NUTR. ABS. (m)

Disturbance of carbohydrate metabolism in stellate cell blockade. IRISGLER (Arch. klin. Chirurg., 1933, 177, 708—715).—After poisoning the stellate cells (I) by intravenous injection of electrocolloidal Cu, there was, in fasting rabbits, an initial hyperglycæmia, followed by a progressive hypoglycæmia, unrelieved by glucose administration, resulting in convulsions and death. There is a close connexion between the liver cells (II) and (I); "blocking" (I) affects (II) and produces the same effect on carbohydrate metabolism as a true liver poison or hepatectomy. NUTR. ABS. (b)

Determination of arsenic [in urine] by Cribier's method.—See this vol., 745.

Detoxication of hydrogen cyanide. W. WIRTH and F. G. LAMMERHIRT (Biochem. Z., 1934, 270, 455—459).—Administration of $Na_2S_2O_8$ or $NaNO_2$ to an animal delays reaction to inspired HCN, and if the dose is sublethal assists in recovery, but if it is lethal, does not assist in keeping the animals alive. P. W. C.

Lactic acid in blood and tissues following intravenous injection of sodium hydrogen carbonate. J. HALDI (Amer. J. Physiol., 1933, 106, 134—144).—Following injection of NaHCO_3 , brain frozen immediately after decapitation has approx. the same lactic acid (I) content as a control brain, but after 5 and 10 min. incubation there is a slight increase. The kidney and muscle of animals receiving NaHCO_3 show a val. $>$ that of controls, but there is a relatively larger increase in the control kidney after incubation. NaHCO_3 invariably produces marked rise in blood-(I) within a few min., and there is increased excretion of (I) in the urine. NUTR. ABS. (m)

Effect of ammonium chloride on the adrenalinic hyperglycaemia and hyperlacticacidemia of rabbits. M. OHARA (Mitt. med. Akad. Kioto, 1933, 9, 443—454).—In normal rabbits simultaneous injection of 10% NH_4Cl with adrenaline increases the rise in blood-sugar and -lactic acid. In splanchnicotomised rabbits the NH_4Cl affects blood-sugar increase only slightly and appears to inhibit increase of -lactic acid. NUTR. ABS. (m)

Mechanism of the hyperglycaemia and high blood-lactic acid in the rabbit following ammonium chloride administration. M. OHARA (Mitt. med. Akad. Kioto, 1933, 9, 979—996).—Narcotisation with amylal reduces the effect of subcutaneous NH_4Cl injection. The rise of blood-sugar is $\frac{2}{3}$ of that found in normal rabbits and the rise in blood-lactic acid is small and variable. Narcotised and normal rabbits show an equal fall in alkali reserve. The modifications of the action of NH_4Cl following section of various nerves are described. NUTR. ABS. (m)

Action of potassium and other ions on the injury potential and action current in *Maia* nerve. S. L. COWAN (Proc. Roy. Soc., 1934, B, 115, 216—260).—The injury potential (I) of *Maia* nerves is 30 mv., which is depressed rapidly and reversibly by KCl. K, Rb, and Cs reduce the action current, but the two latter have little effect on (I). Ca lowers the effects of K, Rb, and Cs. C. G. A.

Influence of chronic fluorosis on vitamin-C in certain organs of the rat. P. H. PHILLIPS and C. Y. CHANG (J. Biol. Chem., 1934, 105, 405—410).—NaF in sufficient amount inhibits growth. Vitamin-C was increased in both the pituitary and adrenal glands, but not affected in the liver or kidney. H. G. R.

Action of harmful dusts. E. H. KETTLE (Bull. Inst. Min. Met., 1934, No. 357, 15 pp.).—A lecture.

Parasitism in heavy water of low concentration. E. J. LARSON and T. C. BARNES (Nature, 1934, 133, 873—874).—When kept in dil. heavy H_2O for long periods *Planaria maculata* (I) and *Phagocata gracilis* show a slower rate of shrinkage in body size probably owing to reduced enzymic hydrolysis. In more conc. heavy H_2O (1:213 H^2 ratio), (I) are rapidly parasitised by moulds. Moulds, chiefly saprophytic, also develop on seeds of *Aquilegia* in 0.47% H^2 cultures. L. S. T.

Physiological effect of trihydrol in liquid water. T. C. BARNES (Science, 1934, 79, 455—457).—A summary. L. S. T.

Radioactivity and metal-protein complexes. I. A. BENEDICENTI. II. G. RASTELLI. III. Biological action of normal and radioactive cobalt. A. GARELLO. IV. Fixation of cobalt in the lungs and its elimination by animals which inhale radium emanation. P. MASCHERPA. V. Effect of radium on cutaneous absorption of metals. A. AMBROGIO. VI. Effect of radium and its emanation on the metallisation of proteins. P. MASCHERPA (Arch. Sci. biol., 1933, 16, 421—422, 423—427, 428—432, 433—440, 441—451, 452—462; Chem. Zentr., 1933, ii, 2852).—II. Ra promotes the metallisation of protein. Radon acts similarly to RaBr_2 .

III. Radioactive Co is much more quickly fatal to the frog than normal Co, probably owing to quicker dissolution in the tissues and to a greater power of diffusion.

IV. Co administered intravenously to animals inhaling Rn is fixed only in small amounts by lung protein. Further inhalation of Rn leads to complete elimination of Co by the kidneys in 2 hr.

V. Ra irradiation promotes absorption of metals through the skin. The smallest Ra doses suffice.

VI. Co powder electrolytically treated with Ra or Rn is much more energetic in its metallising action on protein than is normal Co. Proteins with $p_H >$ the isoelectric p_H react most strongly. Radioactive Co is more poisonous than normal Co. L. S. T.

Mitogenetic radiation and bioluminescence. J. B. BATEMAN (Nature, 1934, 133, 860).—Critical. L. S. T.

Effect of ultra-violet light on blood-phosphorus in the fasting animal. R. DELLA GIUSTINA (Riv. Clin. Pediat., 1933, 31, 1205—1226).—Serum- PO_4 in rabbits on a low-P diet, after a fast of about 15 hr., is increased by ultra-violet irradiation. NUTR. ABS. (m)

Blood-cholesterol in man immediately after irradiation by infra-red rays, sunlight, and rays intermediate between ultra-violet and X-rays. S. MALCZYNSKI and J. LANKOSZ (Compt. rend. Soc. Biol., 1933, 114, 1126—1128).—Increase occurs usually 15 min. after irradiation. Normal vals. are reattained in 24 hr. NUTR. ABS. (m)

Effects of X-rays on *Planaria dorotocephala*. F. G. MESERVE and M. J. KENNEY (Science, 1934, 79, 408—409). L. S. T.

Cytochrome and the oxygen-carrying enzyme. O. WARBURG and E. NEGELEIN (Naturwiss., 1934, 22, 206—207).—The term "cytochrome" is to be reserved for the inert materials described by Keilin in 1925; it cannot be extended to the active O-carrying enzyme (cf. Keilin, this vol., 109, 452). R. K. C.

Cytochrome. E. HAAS (Naturwiss., 1934, 22, 207).—The absorptions of a suspension of baker's yeast at 550 μ under aerobic and anaerobic conditions can be measured photo-electrically, and indicate the concn. of cytochrome (I). When HCN is added the rate of change into the Fe^{II} form of (I) corresponds with the rate of O_2 uptake in a respirometer. The O_2 taken up by the O-carrying enzyme

therefore reacts further in respiration only by way of the cytochrome-Fe.

R. K. C.

An absorption band in the yellow in baker's yeast. O. WARBURG and E. HAAS (Naturwiss., 1934, 22, 207).—A fully-oxygenated suspension of washed baker's yeast shows an absorption band at 583 $m\mu$, which disappears when aëration ceases. This "respiratory" band is attributed to an O-additive product of a Fe^{II} -hæmin compound. CO causes a shift to 590—600 $m\mu$.

R. K. C.

Flavin respiration. T. WAGNER-JAUREGG, H. RAUEN, and E. F. MÖLLER (Z. physiol. Chem., 1934, 224, 67—78).—In the dehydrogenation of glycerophosphoric acid, glyceraldehydephosphoric acid, and particularly succinic acid and PrCHO by rat-muscle and liver pulp, flavin acts as H acceptor. Malic and fumaric acids are inhibitors. Frog's muscle has a much slower action unless a liver extract (I) is added. Washed muscle is inactive even in presence of (I). Unwashed rat-muscle yields succino-dehydrogenase (II) solutions, which in presence of (I) can replace muscle. (I) is best obtained with 50% glycerol (III). The (III) extracts of various organs show decreasing activator-activity in the order liver, kidney, heart, testes, lung, spleen, brain, muscle. (II) activity is suppressed by CO and KCN. The ease of reduction of pyocyanine, flavin, and rosindulin-GG decreases in that order, following the oxidation-reduction potentials.

J. H. B.

Mechanism of the main respiration of pigeon's breast-muscle. B. GÖZSY and A. SZENT-GYÖRGYI (Z. physiol. Chem., 1934, 224, 1—10).—Another co-enzyme in addition to co-dehydrase takes part in the respiration (I) of the minced breast-muscle of the pigeon. (I) is inhibited by malonate and maleate, but accelerated by succinate (II) or fumarate (III) without destruction of (II) or (III). (II) probably acts as catalyst of H transport.

J. H. B.

Oxidising enzymes in betel leaves (*Piper betel*). K. BASU, M. C. NATH, and S. C. CHAKRAVARTY (J. Indian Chem. Soc., 1934, 11, 265—276).—2% $p\text{-C}_6\text{H}_4(\text{OH})_2$ (I), leucine, and succinic acid at p_H about 5 are oxidised by the enzymes of betel juice (II) at 25° and 34.4°; temp. has little effect. MeCHO (III) has its optimum p_H of 6.2, and there is an appreciable temp. coeff. Lecithin accelerates the oxidation of linoleic and retards that of oleic acid. 0.002N-KCN retards oxidation of (I) and (III) to the extent of 75 and 45%, respectively (cf. A., 1929, 219). The catalase of (II) decomposes H_2O_2 at p_H 5.3; HCN retards its action.

J. L. D.

Liver enzymes. II. Aldehydease. L. REICHEL and R. WETZEL (Z. physiol. Chem., 1934, 224, 176—186; cf. A., 1932, 303).—Stable dry preps. of aldehydease (I) are obtained by repeated pptn. of aq. liver extracts with COMe_2 . Determinations of EtOH and EtCO₂H show that (I) produces quant. dismutation of EtCHO at p_H 7.8 under aërobic or anaërobic conditions.

J. H. B.

Decomposition of lactic acid by yeast enzymes. A. HAHN and E. FISCHBACH (Z. Biol., 1934, 95, 155—163).—Lactic acid (I) when treated with yeast extract (II), purified by adsorption on $\text{Al}(\text{OH})_3$, in

presence of methylene-blue (III) in vac. is converted into AcCO_2H and MeCHO. In presence of O_2 no disappearance of (I) occurs. (I), hexosediphosphoric acid, and citric acid strongly increase the O_2 uptake of (II) in the presence of (III); with (I) KCN lessens the increase by 50%. Muscle-extract and lactacidogen produced an increased O_2 uptake, independent of the presence of (III), which could be decreased by KCN to the extent of 70—80%.

H. D.

Lactic acid fermentation. E. AUBEL and E. SIMON (Compt. rend. Soc. Biol., 1933, 114, 905—907).—As dried yeast, COMe_2 extract of dog's muscle, and Thunberg's muscle extract (I) have no action on the system α -glycerophosphate (II)— AcCO_2H but produce from Mg hexose phosphate, AcCHO and lactic acid, it follows that, under the experimental conditions involved, AcCHO, not AcCO_2H , is the precursor of lactic acid. Although (I) contains (II) dehydrogenase, AcCO_2H reduction is not effected owing to the destruction of the Mg adenylyl pyrophosphate.

NUTR. ABS. (m)

Enzymic equilibrium between hexosediphosphoric acid and dihydroxyacetonephosphoric acid. O. MEYERHOF and K. LOHMANN (Naturwiss., 1934, 22, 220).—Dihydroxyacetonephosphoric acid (I), formed from hexosediphosphoric acid (II) (this vol., 560), is identical with the synthetic acid (Kiessling, *ibid.*, 754). The equilibrium, $(\text{II}) = 2 (\text{I})$ in presence of enzyme, allows (II) to be prepared from synthetic (I), and the equilibrium mixture (III) can be obtained either from (II) or (I); the variation of (III) with temp. is identical, whether derived from (II), natural (I), or synthetic (I). Addition of KCN or NaHSO_3 disturbs the equilibrium, and the H sulphite compound of (I) can be obtained in 90% yield.

R. K. C.

Synthesis of a carbon chain by enzymes. V. Occurrence of carboligase in the animal organism. A. STEPANOV and A. KUSIN (Ber., 1934, 67, [B], 721—722; cf. A., 1931, 983).—The carboligase (I) content of the muscle of the dog is \ll that of plants (*loc. cit.*). Traces of (I) are present in the liver. The universal occurrence of (I) in regions of carbohydrate synthesis justifies the assumption that it has a sp. part in the process.

H. W.

Synthesis of a carbon chain by enzymes. VI. Re-synthesis of glycogen in muscle. A. STEPANOV and A. KUSIN (Ber., 1934, 67, [B], 723—726).—In spite of autolysis of glycogen (I), the amount of (I) present after 24 hr. in a solution of K ketohydroxy-succinate (II) in H_2O at p_H 6.4 and 35° containing the striped muscle of the dog is nearly twice as great as in the absence of (II). The amount of monosaccharide (? glucose) is also increased.

H. W.

Amylosynthase. XIX, XX. T. MINAGAWA (J. Agric. Chem. Soc. Japan, 1933, 9, 1198—1202, 1202—1206).—XIX. *iso*Lichenin (I) is present in *Alectoria ochrolenca*, *A. sulcata*, *A. japonica*, *Ramalina geniculata*, and *Usnea trichodea*, but not in *Cladonia bellidiflora*, *Gyrophora vellea*, *Lobaria pulmonalis*, *Parmelia tinctorum*, *Ramalina pollinialis*, *Usnea japonica*, and *U. montis*. Malt amylase or heating

with glycerol converts (I) into a product which does not give the I reaction and cannot be polymerised by amylosynthase (II). (I) closely resembles amylase.

XX. The action of (II) is retarded by $\text{Al}(\text{NO}_3)_3$, $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, AlCl_3 , and FeCl_3 . (II) is reactivated by $(\text{NH}_4)_2\text{SO}_4$. Following treatment with Ag, Cu, Hg, Zn, or Pt salts, (II) could not be reactivated.

CH. ABS.

Fermentation of polysaccharides. E. THILO (Diss., Berlin, 1931; Bied. Zentr., 1934, A, 4, 446).—Tryptic digestion of protein renders it an energetic activator of amylase. The saccharification of cellulose by malt and snail extracts is examined.

A. G. P.

Limits of degradation of starches by the action of salivary and pancreatic amylases. H. J. VONK and J. P. BRAAK (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 188—193).—The action of salivary amylase (man) or pancreatic amylase (pig) on starch causes degradation far beyond the limit (36%) found by van Klinkenberg (A., 1932, 91, 1062; 1933, 92) for malt α -amylase, and the supposition that animal amylases attack only α -starch is untrue.

R. K. C.

Influence of temperature on the stability of ptyalin. R. EGGE (Z. physiol. Chem., 1934, 224, 129—140).—The temp. coeff. (Q_{10}) of ptyalin destruction varies with both temp. and p_{H} . Q_{10} is min. at low p_{H} , when the enzyme is least stable and very sensitive to change in p_{H} , and max. at low temp., where the stability is greatest. The Arrhenius const. A is more const.; it varies with reaction and is max. at the stability optimum.

J. H. B.

Characteristics of intestinal lactase. F. A. CAJORI (Amer. J. Med. Sci., 1934, 187, 295).—A lactose-splitting enzyme is invariably present in aq. extracts of the mucosa of the duodenum and jejunum of adult dogs. The activity of intestinal lactase is max. at p_{H} 5.4—6; it is inhibited by glucose, but not by galactose. Aq. extracts of liver have one third of the lactase activity of intestinal mucosa extracts.

CH. ABS.

Enzyme action. XLVII. Lipase action of serum. XLVIII. Lipase actions of horse serum. G. MCGUIRE and K. G. FALK (J. Biol. Chem., 1934, 105, 373—377, 378—389).—XLVII. Definite differences were found in the hydrolytic action of horse-, rat-, human, sheep-, and ox-serum (in order of descending activity) on different esters.

XLVIII. Horse-serum is suitable for the study of esterase actions and contains > one enzyme. Determinations of $[\text{H}^+]$ of serum should always be checked electrometrically owing to "protein error."

H. G. R.

Activation of papain by vitamin-C (ascorbic acid) or vitamin-C-iron. III. E. MASCHMANN and E. HELMERT (Z. physiol. Chem., 1934, 224, 56—67; cf. this vol., 328).—When vitamin-C+Fe complex (I), papain (II), and substrate (III) are brought into contact, increased activity occurs only after some hr., but it is immediate if (II) is allowed to act on (I) for a time before (III) is supplied. Thiol activators neutralise the antiproteolytic action of heavy metals, (I) has no such effect. Witte's peptone is not hydrolysed by (II) in absence of vitamin-C

(IV), or better (I); gelatin-peptone is hydrolysed, but (IV) alone inhibits, whilst (I) accelerates the action.

J. H. B.

X-Ray photographs of crystalline pepsin.—See this vol., 720.

Preparation of enzymically pure proteinase and determination of the influence of protaminase. L. WEIL (J. Biol. Chem., 1934, 105, 291—299).—Enzymically pure proteinase (I) was obtained by removal of protaminase (II) and carboxypolypeptidase from pig-pancreas extract by adsorption with $\text{Al}(\text{OH})_3\text{-C}_\gamma$ and -A . Acid protone is used as substrate for the determination of (II). (II) is activated by enterokinase. Free NH_2 or CO_2H groups are not necessary for the activity of (I), substitution causing no inhibition.

C. G. A.

Inactivation of pepsin, trypsin, and salivary amylase by proteases. H. TAUBER and I. S. KLEINER (J. Biol. Chem., 1934, 105, 411—414).—Pepsin and trypsin (I) can be reciprocally digested at the correct p_{H} . Erepsin does not digest (I) and salivary amylase is slowly inactivated by (I) and H_2S -papain.

H. G. R.

Effect of decomposition products on enzymic proteolysis. E. DRESSLER (Diss., Berlin, 1931; Bied. Zentr., 1934, A, 4, 446—447).—The inhibitory action of decomp. products (I) on tryptic proteolysis is not observed if the concn. of enzyme is small relative to that of substrate and (I). The combination of enzyme and (I) is probably completely dissociated at low concn. Similar relationships were not apparent in the case of pepsin.

A. G. P.

Action of oxidising and reducing agents on cathepsin. A. V. BLAGOVESTSCHENSKI and I. I. KORMAN (Biochem. Z., 1934, 270, 341—345).—Cysteine, O_2 , and H_2O_2 all inhibit the proteolytic action of cathepsin (from ripening seeds of *Vicia sativa*) on the globulin of sunflower seeds and favour the synthesis of material precipitable by $\text{CCl}_3\text{-CO}_2\text{H}$.

P. W. C.

Mechanism of the action of histozyyme. F. P. MAZZA and L. PANNAIN (Atti R. Accad. Lincei, 1934, [vi], 19, 97—102).—Histozyyme differs from carboxypeptidase by combining, not with the free CO_2H of the substrate, but with the N of the -CO-NH . The difference between its activities towards aliphatic and aromatic acyl derivatives is probably due, not to the existence of two different enzymes, but to the varying velocities of the hydrolyses catalysed by the enzyme. This velocity is lower with the aromatic derivatives, and diminishes as the nucleus coupled with the NH_2 -acid becomes more electro-negative.

T. H. P.

Antagonism of zinc and hydrocyanic acid in their action on peptidase activity. K. LINDERSTRÖM-LANG (Z. physiol. Chem., 1934, 224, 121—126).— Zn^{++} at low concn. ($< 3 \times 10^{-3}N$) activates peptidase, but higher concns. inhibit. HCN inhibits in all cases. Small amounts of Zn reverse the inhibition by HCN owing to combination, but larger amounts inhibit; the curve thus shows a max. corresponding with $\text{Zn}(\text{CN})_4^{--}$. Addition of HCN to a solution inhibited by Zn increases the inhibition.

J. H. B.

Proteolytic enzymes. III. a. Mode of action and specificity of dipeptidase. M. BERGMANN and L. ZERVAS. b. Dipeptides with predominantly acid properties and their behaviour towards enzymes. M. BERGMANN, L. ZERVAS, L. SALZMANN, and H. SCHLEICH. c. Synthesis of dipeptides of lysine and their behaviour towards proteolytic enzymes. d. Dipeptides of epimeric glucosamic acids and their behaviour towards dipeptidase. Configuration of *d*-glucosamine. M. BERGMANN, L. ZERVAS, H. RINKE, and H. SCHLEICH. e. Synthesis of peptides of arginine. M. BERGMANN, L. ZERVAS, and H. RINKE. IV. Specificity and mode of action of so-called carboxy-polypeptidase. M. BERGMANN, L. ZERVAS, and H. SCHLEICH (Z. physiol. Chem., 1934, 224, 11—17, 17—26, 26—33, 33—39, 40—44, 45—51).—IIIa. Introductory. For hydrolysis of dipeptides (I) by dipeptidase (II) the necessary conditions are : the N of the peptide linking must bear H, the two adjacent C atoms (α and α') must bear H, and the α - and α' -C must show a definite configuration. If the imide form is the actual substrate, steric considerations, based on double linking and optical asymmetry, indicate that with (I) of the natural NH_2 -acids when the CO_2H and NH_2 are on the same side of the mol. plane the α - and α' -H atoms are on the other side of the flat (I) mol. and thus allow approach of (II) which is a necessary preliminary to fission.

b. Carbobenzoyloxy-*l*-glutamic acid anhydride with *l*-tyrosine ester (I) gave, as *Et* ester, m.p. 176°, carbobenzoyloxy-*l*-glutamyl-*l*-tyrosine, m.p. 185° (corr.), which on hydrogenation yielded *l*-glutamyl-*l*-tyrosine (II), $[\alpha]_D^{20} + 30.1^\circ$ in $\text{H}_2\text{O} + 1$ mol. HCl. *O*-Acetyl-*N*-carbobenzoyloxy-*l*-tyrosine, m.p. 120—121°, affords the acid chloride (III), m.p. 54°, which with (I) yields *O*-acetyl-*N*-carbobenzoyloxy-*l*-tyrosyl-*l*-tyrosine *Et* ester, m.p. 160—161°, giving, by hydrolysis and hydrogenation, carbobenzoyloxy-*l*-tyrosyl-*l*-tyrosine, m.p. 148° (corr.), and *l*-tyrosyl-*l*-tyrosine (IV), m.p. $+240^\circ$, $[\alpha]_D^{19} + 30.1^\circ$ in $\text{H}_2\text{O} + 1$ mol. of HCl. With Et_2 *l*-aspartate, (IV) gives *Et* *O*-acetyl-*N*-carbobenzoyloxy-*l*-tyrosyl-*l*-aspartate, m.p. 144° (corr.), yielding *N*-carbobenzoyloxy-*l*-tyrosyl-*l*-aspartic acid, and *l*-tyrosyl-*l*-aspartic acid (V), $[\alpha]_D^{19} + 20.4^\circ$ in $\text{H}_2\text{O} + 1$ mol. of HCl. Authentic β -*l*-asparagyl-*l*-tyrosine (VI), synthesised by way of *l*-(α -benzoyl-*N*-carbobenzoyloxyasparagyl)- β -*l*-tyrosine *Et* ester, m.p. 128°, and carbobenzoyloxy-*l*-asparagyl- β -*l*-tyrosine (*Me*₂ ester, m.p. 136°), was identical with the alleged α - (A., 1932, 935), which was therefore actually the β -isomeride. (II) and (V) are, but (VI) is not, hydrolysed by dipeptidase (VII) (since the free NH_2 is not in the α -position); (IV) is the only known dipeptide hydrolysed by both (VII) and trypsin.

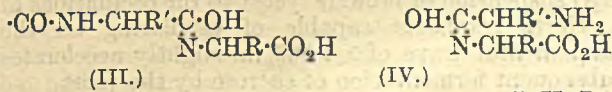
c. *l*-Lysyl-*l*-glutamic acid (I) yields a diphenyl-carbimido-derivative, m.p. 144° (corr., decomp.), hydrolysed to *l*-lysinephenylcarbimidophenylhydantoin, m.p. 195° (corr.), $[\alpha]_D^{20} - 33.7^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and *d*-glutamic acid hydrochloride, thus affording proof of its constitution. The following dipeptides were synthesised by the stages indicated. *l*-(ϵ -Benzoyl-lysyl)-*l*-glutamic acid (II), m.p. 220° (corr.) (decomp.), $[\alpha]_D^{20} + 14^\circ$ in $\text{H}_2\text{O} + \text{HCl}$: ϵ -benzoyl-*l*-lysine, m.p. 262° (corr.) (cf. lit.) $\rightarrow \epsilon$ -benzoyl- α -carbobenzoyloxy-*l*-

lysine, m.p. 99—100° \rightarrow hydrazide, m.p. 191° (corr.) \rightarrow azide \rightarrow *Et*₂ (ϵ -benzoyl- α -carbobenzoyloxy-*l*-lysyl)-*l*-glutamate, m.p. 154° (corr.) \rightarrow free acid, m.p. 173° (corr.) \rightarrow (II). *l*-Lysyl-*l*-aspartic acid (III) ($+\text{H}_2\text{O}$), m.p. 161° (corr.) (decomp.), $[\alpha]_D^{20} + 23^\circ$ in H_2O : dicarbobenzoyloxy-*l*-lysyl hydrazide \rightarrow azide \rightarrow *Et*₂ dicarbobenzoyloxy-*l*-lysyl-*l*-aspartate, m.p. 142° (corr.) \rightarrow (III). *l*-Lysylglycine (IV) [sulphate, m.p. 207.5° (corr.), $[\alpha]_D^{20} + 30.0^\circ$ in H_2O]; dicarbobenzoyloxy-*l*-lysine *Me* ester \rightarrow chloride \rightarrow dicarbobenzoyloxy-*l*-glycine *Et* ester, m.p. 90°, \rightarrow free acid, m.p. 158—159° (corr.) \rightarrow (IV). Lysylglutamic acid liberates its total lysine-N (Van Slyke) in little > 5 min. All the dipeptides were hydrolysed by dipeptidase [(I) only very slowly]; they resisted aminopolypeptidase and trypsin.

d. The following dipeptides were synthesised by the steps indicated. *Et* benzylidene-*d*-glucosamate hydrochloride \rightarrow (carbobenzoyloxyglycyl)benzylidene-*d*-glucosamic acid, m.p. 167—168° (corr.) [lactone, m.p. 197—198° (corr.)] \rightarrow glycyl-*d*-glucosamic acid (I), m.p. 179—180° (corr.), brown at 166°. Carbobenzoyloxy-*l*-phenylalanine, m.p. 126—128° (corr.), $[\alpha]_D^{19} + 4.9^\circ$ in AcOH, \rightarrow acid chloride, m.p. 42°, \rightarrow *Et* (carbobenzoyloxy-*l*-phenylalanyl)benzylidene-*d*-glucosamate, m.p. 173° (corr.), \rightarrow free acid, m.p. 157° (corr.), \rightarrow *l*-phenylalanylbenzylidene-*d*-glucosamic acid ($+\text{H}_2\text{O}$), m.p. 166—167° (corr.) \rightarrow *l*-phenylalanyl-*d*-glucosamic acid (II), m.p. 182° (corr.), $[\alpha]_D^{19} + 40^\circ$ in H_2O . *epi*Glucosamic acid + carbobenzoyloxyglycyl chloride \rightarrow carbobenzoyloxyglycyl-*d*-epiglucosamic acid, m.p. 150—151° (corr.) \rightarrow glycyl-*d*-epiglucosamic acid (III), m.p. about 215°, $[\alpha]_D^{19} - 9^\circ$ in H_2O . (III) is, but (I) and (II) are not hydrolysed by dipeptidase. *d*-epiGlucosamic acid must therefore have the same configuration as the natural (*l*) NH_2 -acids, whilst *d*-glucosamic acid corresponds with the *d*- NH_2 -acids.

e. Hydrogenation of *l*-nitroarginine (I), m.p. 263° (corr.) (cf. lit.) [carbobenzoyloxy-derivative, $+\text{H}_2\text{O}$, m.p. 126° (corr.) (*Me* ester, m.p. 125°)], affords *l*-arginine. With carbobenzoyloxyglycyl chloride, (I) gives carbobenzoyloxyglycyl-*l*-nitroarginine, m.p. 145° (corr.), which on hydrogenation affords glycyll-arginine (II) (diflavianate, $+\text{H}_2\text{O}$, decomp. about 220—225° sulphate, $+\text{H}_2\text{O}$). With arginine in place of (I) the yield of (II) is low.

IV. Methyl-*l*-tyrosine *Me* ester affords chloroacetyl-*N*-methyl-*l*-tyrosine *Me* ester, m.p. 108° (corr.), which on hydrolysis gives chloroacetyl-*N*-methyl-*l*-tyrosine (I), m.p. 135° (corr.), $[\alpha]_D^{19} - 97.7^\circ$ in H_2O . (I) in contrast with chloroacetyl-*l*-tyrosine is not hydrolysed by carboxypolypeptidase (II), indicating that the peptide-H is indispensable for (II) action. (II) reacts with the grouping (III), which is contrasted with the grouping (IV) necessary for dipeptidase action. The two enzymes are thus complementary. Most dipeptides are of type (IV); only the few which can exist in form (III), e.g., *l*-tyrosyl-*l*-tyrosine, are hydrolysed by (II)



J. H. B.

Apparatus for determining the rate of carbon dioxide production during yeast fermentation. K. W. FRANKE and A. L. MOXON (*J. Biol. Chem.*, 1934, **105**, 415—418).—The apparatus automatically records the rate of CO₂ production. H. G. R.

Biochemistry of the pigments of red yeast. H. FINK and E. ZENGER (*Woch. Brau.*, 1934, **51**, 129—130).—Light or darkness had no appreciable effect on the growth of, or amount of pigment developed by, the red yeast investigated (cf. this vol., 562). The most favourable temp. was 20°, whilst growth and amount developed in air were > in O₂, the smallest vals. being obtained for each in N₂. I. A. P.

Polyose of yeast membrane. I. L. ZECHMEISTER and G. TÓTH (*Biochem. Z.*, 1934, **270**, 309—316).—Pressed yeast (1 kg.) after digestion with alkali and acid gave a polyose (15 g.) containing 0.4% ash and 0.3—0.4% N, which on hydrolysis gave a 95% yield of glucose. If the hydrolysis is stopped when 2/3 completed, a disaccharide can be separated as the osazone, m.p. 198°, $[\alpha]_D^{20} = -75.3^\circ$ in EtOH. Hydrolysis of the methylated polyose gave 2:4:6-trimethyl-*D*-glucose. The polyose is therefore composed of a chain of glucose residues linked in the 1:3 positions. P. W. C.

Determination of ergosterol and total sterols in yeast. F. BILGER, W. HALDEN, and M. K. ZACHERL (*Mikrochem.*, 1934, **15**, 119—140).—Gravimetric and colorimetric methods for determination of total sterols are compared. Colorimetric determination by the Liebermann-Burchard reaction is most suitable; using CHCl₃ as solvent, it may be effected photometrically. Ergosterol may be approx. determined colorimetrically, but not photometrically, by means of the Rosenheim-Page reaction (cf. A., 1930, 951) in *trans*- but not in *cis*-[CHCl₂]₂. J. S. A.

Influence of organic dyes on cell and organ function. VI. Mechanism of absorption of dyes by yeast cells. F. AXMACHER and H. NARATH (*Arch. exp. Path. Pharm.*, 1934, **175**, 293—306; cf. A., 1933, 982).—The absorption of both basic [methylene-blue (I)] and acid dyes [trypan-blue (II)] by yeast cells (III) (living, dead, or lipin-free) varies asymptotically with time. With low concns. of (I) and (II) the amount of absorbed (II), but not that of (I), is related to the wt. of cells present; the variations with (I) are probably due to disturbances in the concn. of electrolytes (e.g., H⁺). The bearing of ionic exchange and membrane-potentials and -equivs. on the absorption is discussed. The presence of gelatin or ovalbumin markedly inhibits absorption to an extent dependent on [H⁺]. The diffusion of gases through a fluid membrane is inhibited to a varying extent by the presence of dyes. F. O. H.

Investigations in the region of high frequency. I. Biochemical action of ultra-short electromagnetic waves. F. PIRRONE (*Atti R. Accad. Lincei*, 1934, [vi], **19**, 108—111).—Exposure of an H₂O suspension of brewers' yeast to the oscillations of a Hertz resonator capable of oscillating on the fundamental wave of λ 1.885 m. slightly accelerates subsequent fermentation of sucrose by the yeast. T. H. P.

Cholesterol and fermentations. E. MONTIGNIE (*Bull. Soc. chim.*, 1933, [iv], **53**, 1410—1411).—Cholesterol prevents fermentation of glucose by yeast, is fixed as lactate, m.p. 232—235° (decomp.), during lactic fermentation, and is changed into metacholesterol (I) by butyric fermentation. (I) is not changed into coprosterol by *B. coli* or faecal bacteria. R. S. C.

Influence of oxygen on the antitoxic action of cholesterol on saponins. B. S. LEVIN (*Compt. rend.*, 1934, **198**, 1812—1815).—Experiments at 60° on *Paramecium aurelia* on plates (free access of O₂) and in tubes (limited O₂) show that the inhibiting action of cholesterol (I) (concn. 1/1000—1/32,000) on the toxic effect of saponin (II) (same concn. limits) is notable even when aeration is unrestricted, but with certain concns. of (I)–(II) the degree of aeration is the more important factor. Since reduced (II) is less toxic, it is assumed that a restricted aeration is favourable to the reduction of (II). J. W. B.

Action of fungi on solutions of aldoses and other carbohydrates. IX. A. ANGELETTI and D. PONTE (*Annali Chim. Appl.*, 1934, **24**, 232—236; cf. A., 1933, 1206).—*Penicillium luteum-purpurogenum* and *P. crustaceum* (I) give small amounts of *D*-gluconic acid when grown in presence of dextrin. With (I) the reducing sugars formed are slightly > those originally present, and remain const. for 3 months, the presence of a dextrinase in the mould being thus indicated. Only (I) gives *D*-gluconic acid with sol. starch. No other acids were detected. T. H. P.

Production of gluconic acid by submerged mould growth under increased air pressure. O. E. MAY, H. T. HERRICK, A. J. MOYER, and P. A. WELLS (*Ind. Eng. Chem.*, 1934, **26**, 575—578).—Increase of pressure increases the yield of gluconic acid (I) produced from glucose (200 c.c.; 20% solution) by *Penicillium chrysogenum* when growing totally immersed and aerated in presence of CaCO₃ (5 g.). At 30° and with the quantities stated 80—87% yields of (I) were obtained in 8 days. R. S. C.

Biochemistry of moulds. II. Metabolic product of *Aspergillus melleus*, Yukawa. E. NISHIKAWA (*J. Agric. Chem. Soc. Japan*, 1933, **9**, 772—774).—*Mellein*, C₁₀H₁₀O₃, m.p. 58°, $[\alpha]_D^{25} = -108.15^\circ$ in CHCl₃ (NO₂-derivative, m.p. 183—184°, $[\alpha]_D^{25} = -171.59^\circ$ in CHCl₃), was isolated. CH. ABS.

Chemistry of mould tissue. III. Composition of certain moulds with special reference to their lipin content. L. M. PRUESS, E. C. EICHINGER, and W. H. PETERSON (*Zentr. Bakt. Par.*, 1934, **II**, **89**, 370—377).—On glucose-malt media the lipin content of a no. of moulds was > and the protein content < corresponding vals. on a glucose-inorg. salt medium. The lipins contained free fatty acid (8—70% calc. as oleic acid) and phospholipins. Relationships are traced between the protein, lipin, and carbohydrate contents of *Aspergillus* species. A. G. P.

Nitrogen in *Aspergillus niger* in relation to the quantities of various salts in the culture solution. G. ROSSI and G. SCANDELLARI (*Biochem. Therap. sperim.*, 1933, **19**, 92—98; *Chem. Zentr.*, 1934, **1**,

559).—Aq. glucose containing NH_4NO_3 , K phosphate, and MgSO_4 is a good nutrient for *A. niger*. Absence of NO_3^- or PO_4^{3-} is injurious; MgSO_4 is desirable, but not essential. The presence of small quantities of MnSO_4 favours N fixation. A. A. E.

Proteolytic enzymes of *Aspergillus parasiticus*. M. J. JOHNSON (Z. physiol. Chem., 1934, 224, 163—175).—Aq. extracts of the dried mycelium of *A. parasiticus* grown on skim-milk-glucose medium contain the proteolytic enzymes proteinase (I), carboxy- (II) and amino-polypeptidase (III), and dipeptidase (IV). The culture solution contains much less (II), (III), and (IV), but more (I), than the mycelium. Partial separation of the enzymes was attained by adsorption methods. (III) was obtained practically free from (I), (II), and (IV) by COMe_2 pptn. and alternate adsorption on $\text{Al}(\text{OH})_3\text{-C}_v$ and $\text{Fe}(\text{OH})_3$ at p_H 4. Tri- and tetra-glycine are hydrolysed by yeast- and intestinal (III), but not by the mould-(III). J. H. B.

Phosphatase and phosphatase of *Rhizopus tritici*. F. HEMMI and N. TSUKITARI (J. Agric. Chem. Soc. Japan, 1933, 9, 1382—1393).—Phosphatase was not found; phosphatase may be present. CH. ABS.

***Rhizobium*. I. Effect of nitrogen source on oxygen consumption by *R. leguminosarum*,** Frank. R. H. WALKER, D. A. ANDERSON, and P. E. BROWN (Soil Sci., 1934, 37, 387—401).—Yeast extract increased the growth and O_2 consumption of cultures as compared with those on a N-free medium. Urea, alanine, NH_4Cl , and NaNO_3 had little or no effect. A. G. P.

Specific influence of acidity on nitrogen fixation by *Azotobacter*. D. BURK, H. LINEWEAVER, and C. K. HORNER (J. Bact., 1934, 27, 325—340).—Consumption of N_2 by *Azotobacter* declines from a max. at p_H 7.8 to zero at p_H 6.0. Within these limits the effect of acidity is reversible. Irreversible inactivation occurs only below p_H 5.0. The rate of consumption of fixed N (urea, NH_3 , NO_3^-) shows the same max., and a min. at approx. p_H 4.5, the change over the entire range being reversible. Relationships between O_2 consumption and p_H are of a similar character. The limiting val. (p_H 6.0) for fixation is not affected by differences in $[\text{Ca}^{++}]$, $[\text{Sr}^{++}]$, or N_2 pressure. The N-fixing system ("azotase") and the particular enzyme combining with N_2 ("nitrogenase") are discussed. A. G. P.

Bacteriological examination of soil on a plant-sociological basis. II. *Azotobacter chroococcum* in cultivated soils of the eastern area of the Neusiedlersee. H. WENZL (Zentr. Bakt. Par., 1934, II, 89, 353—369).—*A. chroococcum* (I) was present in all field and vineyard soils in use for > 20—30 years irrespective of their p_H or humus or CaCO_3 contents, but was less general in recently broken soils. Distribution of (I) in soils after inoculation was more rapid in highly org. loams of low CaCO_3 content than in sandy soils poor in humus and nutrients. A. G. P.

Metabolism of some nitrogen-fixing clostridia. W. H. WILLIS (Iowa State Coll. J. Sci., 1933, 8,

231—233).—Anaerobic N-fixing clostridia growing in N_2 on N-free media of initial p_H 6.5—9.5 produced 4.0—4.3 mg. of fixed N per 50 c.c. in 3 weeks; at p_H 5.0, 3.2 mg. were fixed. CaCl_2 and especially CaCO_3 promoted N fixation. If peptone, $(\text{NH}_4)_2\text{SO}_4$, or NaNO_3 was added to the medium glucose was utilised more rapidly, but little or no N was fixed. CH. ABS.

Relationship between the metabolic processes of micro-organisms and the oxido-reduction potential in the medium. I. Denitrifying bacteria. B. ELEMA, A. J. KLUYVER, and J. W. VAN DALFSEN (Biochem. Z., 1934, 270, 317—340).—A medium containing NO_3^- or NO_2^- and EtOH and sown with *Micrococcus denitrificans* under anaerobic conditions using a Au electrode gives reproducible potentials, a reversible oxido-reduction system being established. When actual denitrifying cells are present in a medium containing NO_2^- the potential vals. are dependent only on $[\text{H}^+]$, and when the NO_2^- has disappeared a considerable fall in potential occurs. The effects of H donators and KCN are investigated. P. W. C.

Physiological youth of a bacterial culture as evidenced by cell metabolism. H. H. WALKER, C. E. A. WINSLOW, E. HUNTINGDON, and M. G. MOONEY (J. Bact., 1934, 27, 303—324).—In peptone- H_2O media with or without aeration with CO_2 - and NH_3 -free air *E. coli* exhibits, between the end of the lag period and the beginning of the logarithmic increase (I), a period of high metabolic activity characterised by the rapid transference of $\text{NH}_3\text{-N}$ from cell to medium and increased CO_2 production. Addition of glucose to aerated media results in a somewhat more prompt initiation of (I) and some reduction in yield of NH_3 and CO_2 . The mechanism of these changes is discussed. A. G. P.

Actinomycosis. L. R. VAWTER (Cornell Vet., 1933, 23, 126—149).—Glucose (I), fructose (II), galactose (III), maltose (IV), sucrose (V), and mannitol (VI) were fermented in 1 day, lactose and raffinose (VII) in 4—10 days, and glycerol (VIII) in 14—21 days by various strains of *Actinobacillus*. With xylose (IX) fermentation was slight and irregular; dulcitol (X), inulin (XI), salicin (XII), and arabinose (XIII) were not fermented, and gelatin was not liquefied. Type I *Actinomyces* fermented (I)—(V) and (XII), but not (VI)—(XI) or (XIII). Type II *Actinomyces* may consist of > 1 species. *Corynebacterium pyogenes* resembles *Actinomyces* Type II; it ferments (IX), but not (XII). CH. ABS.

Action of lipolytic bacteria on simple triglycerides and natural fats. M. A. COLLINS (Iowa State Coll. J. Sci., 1933, 8, 187—189).—Bacterial hydrolysis of simple triglycerides becomes more difficult as the mol. wt. increases. Tristearin is unaffected. 159 cultures showed close agreement between lipolytic and proteolytic powers, but not all lipolytic bacteria (I) are proteolytic in litmus milk. (I) are present in ordinary milk, cream, and butter; but not in aseptically drawn milk or in salted butter. CH. ABS.

Influence of culture media on the biological properties of a cellulolytic bacterium. J. POCHON (Compt. rend., 1934, 198, 1808—1810).—After culture in its natural medium for 15 months *Plectridium cellulolyticum*, isolated from ox paunch, has undergone biological modification, and hydrolysis of cellulose (I) can then be effected in aerobic or anaerobic conditions in synthetic media [K, Mg, P, NH_4 salts of org. acids, proteins, and (I)], at p_{H} 8 (CaCO_3).

J. W. B.

Fermentation of glucose by variants of *B. paratyphosus*-B (type Schottmüller) which form no gas from glucose. A. TASMAN and A. W. POT (Biochem. Z., 1934, 270, 349—365).—The production of H_2 , CO_2 , AcOH, HCO_2H , EtOH, lactic and succinic acids by strains of typhoid and paratyphoid organisms is recorded. The typhoid strains effected the same type of reaction as the normal paratyphoid strains, except that the former could not, and the latter could, decompose formed AcOH into $\text{CO}_2 + \text{H}_2$. In those cases where AcOH accumulated, the fermentation was incomplete, only 48—73% of the glucose being metabolised.

P. W. C.

Effect of common salt on the growth of lactic streptococci in milk. F. H. McDOWALL and L. A. WHELAN (J. Dairy Res., 1933, 5, 42—45).—In concns. up to 2% NaCl stimulates, and at > 3% retards, the development of the organisms. Total inhibition is approached with > 6% NaCl.

A. G. P.

Pneumococcus variation. I. Variants characterised by rapid lysis and absence of normal growth under the routine method of cultivation. M. D. EATON (J. Bact., 1934, 27, 271—291).—Effects of temp., CO_2 , p_{H} , and O_2 tension of the growth and lysis of variant forms are examined. A. G. P.

Staphylococcus toxin. P. NÉLIS, J. J. BOUCKAERT, and E. PICARD (Ann. Inst. Pasteur, 1934, 52, 597—644).—A small quantity of glucose in the medium increases the production of the toxin (I), and successive cultures *in vitro* produce a more regular product without loss of toxicity. *In vivo*, (I) produces lesions in many organs with destruction of protoplasm, and death is caused after intravenous injection by cardiac insufficiency. (I) has no action on trypanosomes, and is destroyed by strong acids, cryptotoxic substances, Na oleate, etc. It is concluded that (I) is a single substance. H. G. R.

Clinical investigation of staphylococcal toxin, toxoid, and antitoxin. H. J. PARISH, R. A. Q. O'MEARA, and W. H. M. CLARK (Lancet, 1934, 226, 1054—1057).—Toxins (I) of various strains of *Staphylococcus* vary markedly in potency; light-coloured variants of *S. aureus* strains produce toxins which are more potent than the parent cultures. When rabbit corpuscles are used the combining power of (I) approximates to the hæmolytic val.

L. S. T.

Action of Timothy bacteria on *l*-phosphoglyceric acid. C. CATTANEO (Biochem. Z., 1934, 270, 382—385).—The biochemical conversion of *l*-phosphoglyceric acid into AcCO_2H , already effected by animal cells, lactic acid bacteria, and *B. coli*,

also occurs with acid-fast bacilli, the yield of AcCO_2H being 36% calc. in respect of the initial material or 100% in respect of the amount of ester dephosphorylated. P. W. C.

Lipins of tubercle bacilli. XXXVIII. Synthesis of phthiocol.—See this vol., 776.

Action of constituents of cod-liver oil on tubercle bacilli. P. A. COPPENS (Pharm. Weekblad, 1934, 71, 584—599).—Highly unsaturated fatty acids are chiefly responsible for changing the appearance of, and eventually killing, tubercle bacilli (I) in cod-liver oil suspension. Japanese wood oil has a similar but much less effective action. Vitamin-A and -D are ineffective. Active (I) contain a peroxidase. S. C.

Use of clarified honey in culture media. H. H. HALL and R. E. LOTHROP (J. Bact., 1934, 27, 349—355).—Flocculant matter appearing in honey-agar preps. is eliminated by preliminary warming of dil. honey (50°) with bentonite and subsequent filtration. Clarified honey is suitable for growth of sugar-tolerant yeasts. A. G. P.

Sealing wet preparations. J. E. BARNARD and F. V. WELCH (J. Roy. Microscop. Soc., 1934, 54, 29—31).—Convenient apparatus for sealing wet preps. (material containing virus bodies etc.) by means of paraffin wax or shellac-rosin mixture is described. P. G. M.

Quantitative bacteriological investigations. A. VAN ACKER (Natuurwetensch. Tijds., 1934, 16, 26—31).—Available methods of carrying out bacterial counts are described and discussed. The results obtained by the plate method are always < those given by the Thoma-Steiner method, but \propto the total no. of bacteria present. The latter method gives closely reproducible results and is trustworthy. H. F. G.

Polarographic analysis of bacterial culture solutions. J. KOŘÍNEK and J. BABIČKA (Zentr. Bakt. Par., 1934, II, 89, 497—501).—The formation of decomp. products of carbohydrates by bacteria is examined by means of the polarograph. A. G. P.

Fungi and fungicides. T. HARADA (Bull. Chem. Soc. Japan, 1934, 9, 186—191).—The fungicidal activity of a no. of chemicals towards *Tricophyton interdigitale*, *T. violaceum*, *Epidermophyton inguinale*, and *Aspergillus oryzae* (I) was investigated. HgI_2 , I, and HgCl_2 are the most potent, whilst (I) will grow in an 8% solution of NaOBz, and a 20% concn. of NaCl is required to prevent growth. $\text{CS}(\text{NH}_2)_2$ is toxic to the fungi, but harmless to human tissue. In some cases acidity alone is responsible for inhibition of growth. AcOH is more toxic than lactic acid. P. G. M.

Fungicidal quality of olive oil ozonide. T. HARADA (Bull. Chem. Soc. Japan, 1934, 9, 192—197).—The product obtained by passing O_3 into olive oil for 120—200 hr. became colourless on keeping for several days and contained 0.37—0.86% of available O. It is more effective in destroying certain fungi than either H_2O_2 or NaOCl, and is suggested for use in the treatment of ringworm. P. G. M.

Toxic effect of sodium iodoacetate on trypanosomes. C. V. SMYTHE and L. REINER (Proc. Soc. Exp. Biol. Med., 1933, 31, 289—292).—0.001M- $\text{CH}_2\text{I}\cdot\text{CO}_2\text{Na}$ (I) destroys a suspension of *T. equiperdum* (II) in 2—3 min. A 240-g. rat tolerates up to 0.2 c.c. of a 0.25M solution of (I); this dose in a rat injected with (II) clears the blood of (II) for 2—10 days. The toxicity of (I) for (II) is uninfluenced by cysteine or thioglycollate; a strain of (II) resistant to As was not resistant to (I). H. D.

Sterilising action of acids. IV. Unsaturated monobasic acids. V. Dibasic aliphatic acids. S. TETSUMOTO (J. Agric. Chem. Soc. Japan, 1933, 9, 761—767, 1284—1293).—IV. Acrylic and crotonic acids have approx. equal sterilising powers at the same mol. concn. That of undecenoic acid and undecenoate is high. The sterilising action of unsaturated acids is generally > that of saturated acids in the same concn.

V. Of dibasic acids, $\text{H}_2\text{C}_2\text{O}_4$ has the strongest action. For C_2 — C_3 the dibasic are stronger than the monobasic acids; for C_6 onwards the reverse holds. No relation was found between the no. of CO_2H groups and the sterilising action. CH. ABS.

Action of ultra-violet rays from a mercury lamp on the cells of *B. mycoides*, Fl. G. A. NADSON and E. A. STERN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 51—56).—Irradiation of young cultures (24 hr.) of *B. mycoides* causes first the (reversible) formation of vacuoles, followed successively by (irreversible) dissociation of the lipoprotein plasma complex, granulation (fat drops) of the plasma and plasmolysis, the cells becoming irregular in shape, and finally forming aggregates of dead and dying bacteria. Similar, but slower, changes are produced by X-rays. J. W. B.

Distant action of metals on the structure and development of *Bacillus mycoides*, Fl. E. A. STERN and A. S. KRIVISKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 254—258).—Retardation of growth and marked changes in morphology occur when cultures are near (approx. 1 mm. from) sheets of Pb, Au, Pt, or Mg; the extent of the action \propto the at. no. of the metal, i.e., $\text{Pb} > \text{Pt}, \text{Au} > \text{Mg}$. F. O. H.

Biological action of metals at a distance. V. RIVERA (Atti R. Accad. Lincei, 1934, [vi], 19, 432—436).—This action is regarded as due to secondary radiation acting either directly on the dividing cells or indirectly on the air of the chamber, possibly by producing ionisation. T. H. P.

Hormones and their chemical relations. E. C. DODDS (Lancet, 1934, 226, 931—935, 987—992, 1048—1054).—Lectures. L. S. T.

Pupation of flies initiated by a hormone. G. FRAENKEL (Nature, 1934, 133, 834).—Pupation in *Calliphora erythrocephala* is initiated by a hormone. L. S. T.

Substances affecting the circulation. I. Method. F. LANGE and I. DONOMAE (Arch. exp. Path. Pharm., 1934, 175, 176—181).—A manometric method for the determination of the vol. of a section of isolated surviving artery and its application to the

study of vaso-constricting and -dilating substances are described. F. O. H.

Influence of the spleen on sulphur metabolism. K. IWABUCHI (Sei-i-kwai Med. J., 1933, 52, No. 4, 59—83).—The spleen plays an important part in the S metabolism of dogs; its activity depresses S metabolism and its absence accelerates it. Injection of opostatin reduces the S metabolism accelerated by splenectomy. Adrenaline and oophormin accelerate S metabolism, especially of splenectomised animals. CH. ABS.

Effect of splenic substances on blood-cholesterol. E. SCHLIEPHAKE (Klin. Woch., 1933, 12, 1936—1938).—Human serum-cholesterol (I) is usually increased by administration of the spleen hormone, prosplen, the increase being the greater the lower is the initial val. (I) is always increased initially by intravenous, but often decreased by intramuscular injection. NUTR. ABS. (m)

Functions of the adrenal cortex. F. A. HARTMAN (Ohio J. Sci., 1934, 34, 4—8).—Cortin given to guinea-pigs on a diet deficient in vitamin-C delayed the onset of scurvy. The adrenal cortex contains cortilactin, necessary for milk production, as well as cortin, a general tissue hormone. CH. ABS.

Influence of adrenaline on blood-potassium. J. L. D'SILVA (J. Physiol., 1933, 80, 7r).—Intravenous injection of 0.5 c.c. of 1:10,000 adrenaline into chloralosed cats causes an increase (up to 65%) in serum-K, the val. returning to normal after 15 min. The K enters the blood-stream from the tissues. NUTR. ABS. (m)

Adrenaline, lymphatic gland extracts, and the hyperglycaemic reaction. M. COPPO (Boll. Soc. ital. Biol. sperim., 1933, 6, 378—381; Chem. Zentr., 1934, i, 560).—Thymus total extract causes hyperglycaemia (I) and diminishes or arrests adrenaline (I). Lymphatic gland extract behaves similarly. A. A. E.

Anterior pituitary hormones. VI. Deamination processes. R. AGNOLI (Boll. Soc. ital. Biol. sperim., 1933, 6, 754—756; Chem. Zentr., 1934, i, 560).—Agnoli's lipid hormone and Zondek's prolan, but not "praephyson," intensify deamination. A. A. E.

Insulin and adrenaline. M. W. GOLDBLATT (J. Physiol., 1933, 79, 286—300).—In the starving young rabbit, insulin (I) and adrenaline produce an increase in liver-glycogen (II). With (I) there is usually an increase in the total glycogen of the body with or without a decrease in muscle-glycogen (III). With adrenaline, in non-glycosuric doses, the increase in (II) is invariably accompanied by a decrease in (III) which may be similar in quantity; with larger doses, both (II) and (III) are diminished. Ergotamine (5 mg. intravenously) does not prevent these changes. $\text{CH}_2\text{I}\cdot\text{CO}_2\text{Na}$ (15 mg.) prevents accumulation of (II). Injection of (I) is not followed by a sufficient increase in blood-lactate to justify the belief that it causes production of (II) through adrenal secretion. NUTR. ABS. (m)

Effect of diet, insulin, and thyroxine on the adrenaline content of the adrenals. H. A. F. GOHAR (J. Physiol., 1933, 80, 305—313).—In white

rats the adrenaline content (I) and wt. of the adrenals are unaffected by high-protein diet, but fat diet leads to a diminution of the abs. (I) and total wt. of the glands; the relative (I) per g. of gland is also slightly diminished. Carbohydrate diet also produces a diminution of the abs. (I); the wt. of the adrenals is diminished so that the relative (I) per g. of gland is increased. Starved rats also show diminution of (I) of the adrenals. Repeated administration of insulin in subconvulsive doses leads to increase in the wt. of the glands and of their (I). In convulsive doses there is a depletion of (I). This effect of insulin is produced through the nervous system as well as by peripheral action on the adrenals. Repeated injection of thyroxine also produces an increase in wt. and (I).

NUTR. ABS. (m)

Correlation between the action of insulin and adrenaline on muscle- and liver-glycogen. K. M. DAOUD and H. A. F. GOHAR (J. Physiol., 1933, 80, 314—322).—Injection of convulsive doses of insulin into rats results in almost complete depletion of the liver-glycogen (I) and considerable diminution of the muscle-glycogen (II). In adrenalectomised animals, insulin causes a similar diminution in (I), but apparently has no effect on (II). Injection of adrenaline also causes depletion of (I) and considerably diminishes (II). The depletion of (I) is determined by the synergetic action of insulin and adrenaline, either of them alone giving the same result as both together, whilst the depletion of (II) is brought about by the insulin by acting indirectly through increased activity of the adrenal glands. A polarimetric method for determining small amounts of glycogen is described.

NUTR. ABS. (m)

Insulin and glycogen. III. F. RATHERY, S. GILBERT, and Y. LAURENT (Ann. Physiol. Physicochim. biol., 1932, 8, 492—593).—Insulin has a const. effect on blood-sugar and a variable effect on liver- and muscle-glycogen. Liver-glycogen in normal, starved, phloridzinised, or depancreatized dogs usually falls. Changes in liver are > those in muscle and are not related to those in muscle or in blood.

NUTR. ABS. (m)

Rôle of the pancreas in the tissue storage of glucose. A. BAISET, L. BOUISSET, L. BUGNARD, J. J. ROUZARD, and C. SOULA (Compt. rend. Soc. Biol., 1933, 114, 1308—1309).—The arterial and venous blood-sugar differences in the limbs of dogs, both normal and depancreatized, receiving glucose intravenously, indicate that the secretion of the pancreas permits storage of glucose in the tissues.

NUTR. ABS. (m)

Effect of insulin on blood-calcium. A. CABITTO (Riv. Clin. Pediat., 1933, 31, 1343—1350).—Insulin increases total blood-Ca and the increase seems to be directly related to the dose. Colloidal Ca is increased relatively more than ultrafilterable, which is increased only by doses of < 1.5—2 units per kg. Hence there is a % reduction in ultrafilterable and a relative increase in colloidal Ca. NUTR. ABS. (m)

Control of the insulin output of the pancreas. T. KOSAKA (J. Physiol., 1933, 79, 416—422).—Infusion of glucose into the pancreatico-duodenal artery of the decapitated cat is followed by a fall of

blood-sugar more rapid than that found when similar injections are made into the femoral artery or portal vein. The pancreas responds to hyperglycæmia of its arterial supply by a liberation of insulin.

NUTR. ABS. (m)

Inactivation of insulin by normal and diabetic blood. P. T. BLACK (Brit. J. Exp. Path., 1933, 14, 318—322).—Insulin incubated with serum, laked red blood-cells, or cytolysed leucocytes, but not with heparinised whole blood or with intact red blood-cells or leucocytes, loses some of its power to lower the blood-sugar level. Blood from diabetics, including that from those resistant to insulin, does not differ in these respects from normal blood.

NUTR. ABS. (m)

Hypercalcæmic action of intravenous injection of potassium chloride in thyroparathyroidectomised animals. J. T. RICO (Compt. rend. Soc. Biol., 1933, 114, 847—848).—When the injections are made a few hr. (but not several days) after removal of the glands a slight increase in serum-Ca results.

NUTR. ABS. (m)

Effect of parathyroidectomy on blood-calcium. R. GREGOIRE, LYONNET, and DELAVENNE (Le Sang, 1933, 7, 790—802).—In dogs, blood-Ca falls from 12.7 to 6.2 mg. per 100 c.c. in 48 hr. and returns to normal in a few weeks. The parathyroids are therefore not alone in their action on carbohydrate metabolism. Chloralose anaesthesia alone reduces blood-Ca by 20%.

NUTR. ABS. (m)

Effect of thyroxine on blood-calcium. C. ROSSO (Riv. Clin. Pediat., 1933, 31, 1351—1359).—Thyroxine always reduces blood-Ca after a slight initial rise. Changes in colloidal Ca closely follow those in total Ca, whilst ultrafilterable Ca shows a variable degree of reduction. In the first period (about 20 min.) ultrafilterable is changed into colloidal Ca.

NUTR. ABS. (m)

Effect of thyroidectomy and thyroid feeding on milk secretion and milk-fat production of cows. W. R. GRAHAM, jun. (J. Nutrition, 1934, 7, 407—429).—Thyroidectomy and also the removal of desiccated thyroid gland from the ration of thyroidectomised cows lowered the total milk and fat yields.

A. G. P.

Non-thyroid substances with thyroid action.
 II. Influence of the fission products of artificially iodised protein (homothyroxine) on avian plumage and body-temperature of guinea-pigs.
 III. Physiologically active substances containing iodine from artificially iodised protein. I. ABELIN (Arch. exp. Path. Pharm., 1934, 175, 146—150, 151—155).—II. The I-containing products of the hydrolysis of iodised protein (homothyroxine) (cf. A., 1933, 1087) act similarly to thyroid preps. in causing moulting and depigmentation of fowls' feathers and in inhibiting the depression of the body-temp. of guinea-pigs due to novocaine.

III. Hydrolysis of iodised caseinogen with aq. Ba(OH)₂ or NaOH followed by pptn. with HCl and extraction with BuOH yields a fraction containing up to 30% I and approx. 4% N which resembles thyroid gland preps. in its action on the basal meta-

bolism of rats and thyroxine-containing fractions of thyroid proteins in its chemical properties.

F. O. H.

Relation of the pituitary gland to the action of insulin and adrenaline. A. B. CORKILL, H. P. MARKS, and W. E. WHITE (*J. Physiol.*, 1933, 80, 193—205).—After removal (I) of the pituitary, rabbits may develop spontaneous hypoglycæmia, and always show greater hypoglycæmic response to insulin, which is but little affected by injection of adrenaline (II) or vasopressin. There is generally also diminished response to (II) and increased sugar tolerance. Neither depletion of the liver-glycogen (III) nor deficient secretion of (II) is responsible for this abnormal sensitivity to insulin. (III) develops an unusual resistance to mobilisation by (II), possibly connected with the observed thyroid and adrenal cortex degeneration after (I).

NUTR. ABS. (m)

Pressor and insulin-antagonistic action of tonephin or pitressin and orasthin. H. SCHROEDER (*Klin. Woch.*, 1933, 12, 1766—1768; *Chem. Zentr.*, 1934, i, 560).—The pressor constituent of pituitary extract raises the blood-sugar (I) and is antagonistic to insulin. The component affecting the uterus has no action on (I).

A. A. E.

Effect of the pituitary gland on nitrogen metabolism. Y. TAKEUCHI and Y. TOKIZAKI (*Sei-i-kwai Med. J.*, 1933, 52, No. 3, 25—50).—Hypophysectomy in dogs produces a slight decrease in urinary non-protein-N, creatine, and creatinine, and blood-N, but an increase, followed by a decrease, in blood-non-protein-N. Daily injection of pituitrin into normal dogs causes a decrease in all except blood-N, and in blood-creatinine and -creatinine; injection into hypophysectomised dogs causes an increase in all cases.

CH. ABS.

Depression of the basal metabolism of thyroidectomised guinea-pigs by anterior pituitary gland. W. SCHOEDEL (*Arch. exp. Path. Pharm.*, 1934, 175, 233—240).—Administration of anterior pituitary preps. (I) to thyroidectomised guinea-pigs (II) produces a diminution in the basal metabolism (III) which is not due to the thyroidectomy. Injection of muscle extracts or of deproteinised, heated (I) has no action on (III). With (II), the (III) of which has been increased by administration of thyroxine, the decrease of (III) by (I) is less evident. The mechanism is discussed.

F. O. H.

Separation of the hormone of the anterior pituitary gland related to fat metabolism from the thyrotropic hormone. K. J. ANSELMINO and F. HOFFMANN (*Arch. exp. Path. Pharm.*, 1934, 175, 335—338).—Ultrafiltration through collodion membranes of suitable extracts of anterior pituitary gland yields thyrotropic hormone (I) (residue) (A., 1933, 1337) and a hormone (II) (ultrafiltrate) which increases the blood-ketones of normal or thyroidectomised rats. Thus the action of (II) on fat metabolism, unlike the ketogenic action of (I), does not depend on the presence of the thyroid gland.

F. O. H.

Crystalline oestrus-producing hormone from horse (stallion) urine. V. DEULOFEU and J.

FERRARI (*Nature*, 1934, 133, 835).—Rhomboid plates, m.p. 254—255°, of high oestrogenic activity and apparently identical with the hormone of the urine of pregnant women, have been isolated from horse urine (cf. this vol., 567).

L. S. T.

Crystalline forms and m.p. of α -follicular hormone. A. KOFLER and A. HAUSCHILD (*Z. physiol. Chem.*, 1934, 224, 150—154).— α -Follicular hormone exists in three cryst. modifications, rhombic metastable (I), m.p. 254°, n_D^{20} 1.594, n_D^{25} 1.628, n_D^{30} 1.647; monoclinic metastable (II), m.p. 256°, n_D^{20} 1.520, n_D^{25} 1.642, n_D^{30} 1.690; and rhombic stable (III), m.p. 259°, n_D^{20} 1.512, n_D^{25} 1.619, n_D^{30} 1.692. (II) is obtained from a conc. solution in 20% EtOH, (I) on evaporation of MeOH solutions, (III) not from solution but from (I) and (II) at approx. the m.p.

J. H. B.

Substance from mammary adenocarcinomata of mice, which increases growth and accelerates genital development in young rats. H. DOBROVOLSKAIA-ZAVADSKAIA and P. ZEPHIROV (*Compt. rend.*, 1934, 198, 1950—1952).—An H₂O-sol., alkalisable substance isolated from adenomatous growths in mice, when injected into young rats, increases the rate of growth and size of uterus and causes early oestrus.

R. S. C.

Relationship of blood-cholesterol to activity of sex glands. J. DIDRY (*Compt. rend. Soc. Biol.*, 1933, 114, 1080—1081).—Differences in serum-cholesterol in dogs following castration and ovariectomy are small and cannot be compared with the much larger variations following thyroidectomy.

NUTR. ABS. (m)

Effect of corpus luteum on blood-calcium in bitches with chronic parathyroid insufficiency. F. MATHIEU (*Compt. rend. Soc. Biol.*, 1933, 114, 1373—1374).—Corpus luteum injections cause a fall in blood-Ca.

NUTR. ABS. (m)

Blood-iodine after castration in bitches. M. FRANKE and L. PTASZEK (*Compt. rend. Soc. Biol.*, 1933, 114, 1129—1130).—In young bitches a transitory increase in blood-I occurs during the first week after oörectomy, followed by a fall. In old bitches there is an initial fall.

NUTR. ABS. (m)

Blood-iodine after castration in dogs. M. FRANKE and L. PTASZEK (*Compt. rend. Soc. Biol.*, 1933, 113, 1302—1303).—Six days after castration blood-I is considerably > before operation. The val. then falls and at 6 weeks is < pre-operative val.

NUTR. ABS. (m)

Formation of a substance which possesses the physiological action of the male hormone. W. DIRSCHERL and H. E. VOSS (*Naturwiss.*, 1934, 22, 315).—Hydrogenation of crude or cryst. samples of follicular hormone yields a product containing the male sex hormone (1 capon unit and 1 mouse unit in 25—100 $\times 10^{-6}$ g.). The original hormone contained 1 capon or mouse unit in 2 mg. (cf. A., 1933; 755).

W. O. K.

Active and inactive forms of the hormone promoting comb-growth. A. A. ADLER (*Nature*, 1934, 133, 798).—The hormone is present in the urine of men in an inactive form (I) which can be extracted

by means of BuOH. (I) is converted into an active form by boiling the extract with $\text{CCl}_3\cdot\text{CO}_2\text{H}$.

L. S. T.

A provitamin-A other than carotene? E. BOYLE (Nature, 1934, **133**, 798).—Spectrographic and colorimetric tests of a turbot concentrate after irradiation show that the chromogen responsible for the 565 $\text{m}\mu$ band is the precursor of the 575 $\text{m}\mu$ chromogen, which is either a vitamin-A purer than that of Carr and Jewell, or is a sterol with higher spectroscopic and colorimetric vals.

L. S. T.

Stability of carotene in olive oil. R. G. TURNER (J. Biol. Chem., 1934, **105**, 443—454).—0.2% of carotene in olive oil or Et laurate together with a stabiliser (I) loses approx. 50% of its vitamin-A activity in 12 months. Light and temp. up to 37° have no effect on this inactivation, but cold prevents it. Without (I) complete destruction occurs in 3—4 months.

H. G. R.

Rich source of β -carotene. W. L. BROWN (Science, 1934, **79**, 481).—The Perfection pimento is a rich source of β -carotene, apparently free from α -carotene. Dried pimento shells contain 200—665 mg. per kg.

L. S. T.

Physico-chemical studies of complex organic molecules. I. Monochromatic irradiation. F. P. BOWDEN and C. P. SNOW. II. Absorption at low temperatures. F. P. BOWDEN and S. D. D. MORRIS (Proc. Roy. Soc., 1934, **B**, **115**, 261—273, 274—278).—Radiations longer than 3130 Å. have no effect on calciferol (I), which is destroyed at 2650 and, less quickly, at 2537 Å. Ergosterol is converted into (I) at 2967 Å. Vitamin- B_1 has an absorption band at 2600 Å. Carotene irradiated at 2650 Å. gave the vitamin-A absorption band at 3280 Å.

II. The bands of β -carotene at liquid air temp. (I) narrow and shift to 4990, 4670, and 4350 Å. with a new band at 4060 Å. The main band of vitamin-A (II) shifts to 3350 Å. and new bands appear at 2900, 2770, 2580, 2510, and 2430 Å. Irradiated carotene, with an absorption band resembling that of (II) at room temp., shows bands at 3780, 3570, 3410, and 3210 Å. at (I); the two substances are thus not identical.

C. G. A.

Absorption spectra of α - and β -carotene and leaf-xanthophyll at room and liquid nitrogen temperatures. E. S. MILLER (Plant Physiol., 1934, **9**, 179).—At the lower temp. of observations the absorption bands become narrower, but more distinct. The max. for carotenoids are moved 165—200 Å. towards the infra-red.

A. G. P.

Differences between biologically active substances before and after isolation from the raw materials in which they occur. H. I. WATERMAN and C. VAN VLODROP (Rec. trav. chim., 1934, **53**, 670—671).—Distillation of carotene (I) in red or colourless palm oil in a cathode vac. with internal condensation gives a distillate richer in (I). This does not occur with natural (II) or pre-conc. (i.e. extracted and fractionally frozen) (III) palm oil. The distillation residue from (II) contains an unaltered % of (I), that from (III) less. However, redistillation (which occurs without decomp.) of the distillate

from (II) causes concn. of (I) in the distillate. It is thus inferred that (I) does not occur entirely in the free state in (II).

R. S. C.

Absorption spectra in oil research. Distillation of palm oil. L. J. N. VAN DER HULST (Rec. trav. chim., 1934, **53**, 672).—Quant. measurement of the absorption spectra shows that distillation of carotene (I) in palm oil (II) concentrates (I) into the distillate, but that this effect is very slight with natural (II) alone (cf. preceding abstract). Bleaching earth (Terrana "superior") absorbs carotene and other pigments from (II) in C_6H_{14} , giving an oil with a spectrum which from λ 220 to 500 $\text{m}\mu$ resembles that of a mixture of oleic and stearic acids.

R. S. C.

Determination of carotene in butter-fat. H. M. BARNETT (J. Biol. Chem., 1934, **105**, 259—267).—A spectrophotometric method for the determination of the carotene (I) content of butter-fat (II) is based on transmittancies at different wave-lengths of varying amounts of (I) dissolved in (II).

A. E. O.

Influence of the nature and amount of proteins in the basal diet on avitaminosis-A. L. RANDOIN and S. QUEUILLE (Compt. rend., 1934, **198**, 1942—1944).—Yeast and caseinogen (I) in the basal vitamin-A-free diet do not affect the onset of xerophthalmia. Large amounts of (I), however, prolong the periods of growth and survival.

R. S. C.

Vitamin-A and -D activity of egg yolks of different colour concentrations. B. BISBEY, V. APPLEBY, A. WEIS, and S. COVER (Missouri Agric. Exp. Sta. Res. Bull., 1934, No. 205, 32 pp.).—Although some relationship exists between the growth of rats and the yolk colour of eggs used in feeding them, the vitamin-A activity of yolks cannot be explained on the basis of their carotenoid pigment contents, but is directly dependent on the hen's ration. Differences in yolk colour cannot be correlated with differences in vitamin-D content.

A. G. P.

Spectrographic evaluation of solutions of vitamin-D in fatty oils. II. L. FUCHS and Z. BECK (Pharm. Presse, 1933, **38**, 93—104; Chem. Zentr., 1933, ii, 2867).—Vitamin-D (I) dissolved in olive oil can be isolated unchanged with the unsaponifiable fraction (II) and by methods previously described (this vol., 333) can be determined more simply than by animal tests. The extinctive power of (II) can be disregarded. Dissolution of (I) in sesamé oil is unfavourable. The presence of white P does not change the (I) in oil solutions.

L. S. T.

Biological comparison of vitamin-D from fish-liver-oils with that from irradiated ergosterol. O. DALMER, F. VON WERDER, and T. MOLL (Z. physiol. Chem., 1934, **224**, 86—96).—Excessive doses of vitamin-D concentrates from halibut- and tunny-liver-oil from which most of the vitamin-A has been removed by maleic anhydride produce the same toxic symptoms in mice as overdoses of irradiated ergosterol or calciferol. The therapeutic indices are also of the same order.

J. H. B.

Action of viosterol and parathormone. J. W. SPIES, R. H. WILSON, and J. A. STRINGHAM (Chinese

Med. J., 1934, 48, 352—372).—In thyroparathyroid-ectomised dogs viosterol (I) and parathormone (II) increase serum-Ca in amounts parallel to the muscular response to stimuli and to the urinary excretion of Ca. (I) produces a positive balance of Ca and P due to diminution of the faecal excretion being > the augmentation of urinary output, whereas (II) produces a negative balance due to the increase in urinary excretion.
H. G. R.

Mustard oil in subacute poisoning by vitamin-D. G. ORZECOWSKI and E. SCHREIBER (Arch. exp. Path. Pharm., 1934, 175, 265—283).—Crude mustard oil (I) has no influence on the changes (calcification etc.) in the arteries of rabbits due to administration of vitamin-D. Large doses of (I) do not influence the gaseous metabolism of rats, whilst during the loss in body-wt. preceding death in rabbits, the urinary excretion of neutral S attains pathological vals.
F. O. H.

Peroxidase reaction. XXXVIII. Relation between Arakawa's reaction and suitability of human milk. K. ASAKURA (Tōhoku J. Exp. Med., 1932, 19, 275—281).—Mice fed on polished rice were protected from vitamin-B deficiency by milk which gave Arakawa's peroxidase reaction, but not by other milk.
Ch. Abs.

Results of administration of large amounts of vitamin-B. G. BAGNACCI (Biochem. Terap. sperim., 1932, 19, 295—307; Bied. Zentr., 1934, A, 4, 344).—Considerable amounts of vitamin-B (up to 400 units) were not detrimental to the health of rats, mice, or pigeons.
A. G. P.

Vitamin-B₁ deficiency in carbohydrate-free diets and the behaviour of ethyl alcohol towards vitamin-B₁. T. ARIYAMA (J. Agric. Chem. Soc. Japan, 1933, 9, 1045—1048).—Addition of autoclaved yeast did not prevent vitamin-B₁ deficiency. Glucose accelerated, whilst EtOH delayed, the appearance of the symptoms.
Ch. Abs.

[Isolation in] larger yields of crystalline anti-neuritic vitamin. R. R. WILLIAMS, R. E. WATERMAN, and J. C. KERESZTESY (J. Amer. Chem. Soc., 1934, 56, 1187—1191).—Details are given for the isolation of the vitamin (as hydrochloride) in a yield of about 5 g. per ton of rice polishings, i.e., about 25% of the amount originally present. The process gives consistent results.
H. B.

Vitamin-B₂. B. C. GUHA and P. N. CHAKRAVORTY (J. Indian Chem. Soc., 1934, 11, 295—310; cf. this vol., 461).—Ox-liver extract (I) (prep. described) at p_H 1.2—11 is not freed completely from vitamin-B₂ (II) when shaken with C. MeOH-HCl is the best reagent for eluting (II). SiO₂ gel and AgBr, but not BaSO₄, adsorb (II) (cf. A., 1931, 988), which is eluted by boiling HCl. (II) is not pptd. by saturated Cu(OAc)₂, HgCl₂, or Br. Fractional pptn. of (I) with MeOH affords the active constituents, whereas with EtOH only partial pptn. occurs; PrOH destroys the activity of (II). Many sugars, cytosine, and irradiated adenine and guanine contain no (II).
J. L. D.

Vitamin-B₂ potency of purified liver preparations. E. BRAND, R. WEST, and C. J. STUCKY

(Proc. Soc. Exp. Biol. Med., 1933, 30, 1382—1384).—Purified liver extracts, potent in pernicious anæmia, did not induce growth in rats deficient in vitamin-B₂.
Ch. Abs.

Vitamin-B₂ in saké and saké-kasu (pressed cake). F. INUKAI, T. HIGASI, and W. NAKAHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 113—118).—Saké and pressed cake are good sources of vitamin-B₂ (I), which may be obtained from acid MeOH extracts by adsorption on "acid earth." The (I) content of saké yeast is approx. the same as that of brewer's yeast. Neither of these products contains vitamin-B₁.
P. G. M.

Alkali-labile ring of lactoflavin. R. KUHN and H. RUDY (Ber., 1934, 67, [B], 892—898).—Treatment of lumilactoflavin (I) with Ba(OH)₂-H₂O at 100°, acidification of the solution with AcOH, extraction with CHCl₃, and treatment of the extract (II) with NaHCO₃ gives the acid (III) C₁₂H₁₂O₃N₂, m.p. 215° (corr.), yielding a sublimate, m.p. 173—174° (corr.), identical with that obtained by use of NaOH. (III) contains 1 active H (Zerevitinov), is titrated as a monobasic acid in presence of phenolphthalein, and gives a yellow Ag salt sparingly sol. in EtOH-CHCl₃. Na₂S₂O₄ decolorises the yellow solution in EtOH, but the colour is restored by air. Extraction of (II) with Na₂CO₃ gives a substance, partial decomp. 370° (red Ag salt); the colour of its solution darkens on addition of NaOH. Zn and HCl give a red intermediate. Reversible decolorisation is effected with difficulty by Na₂S₂O₄. Treatment of (II) with NaOH gives unchanged (I). Since 2H₂O are required for the alkaline hydrolysis of (I) the group which yields urea must belong to a ring system; this view is confirmed by the great stability of (I) towards HNO₂. Unsuccessful attempts at de-amination and acetylation indicate that both O atoms of (I) belong to the alkali-labile ring. 2 CO must therefore be involved, one of which appears as urea, whilst the other leads to CO₂H in (III). Treatment of the Ag salt of (I) with MeI yields a Me₁ derivative, sol. in NaOH, whereas (I) and Me₂SO₄ give a Me₂ compound, insol. in NaOH; both resemble (I) closely in colour and fluorescence.
H. W.

Dissociation constants of flavins. Relationship of p_H and fluorescence. R. KUHN and G. MORUZZI (Ber., 1934, 67, [B], 888—891).—The p_H -% of max. fluorescence graph of vitamin-B₂ (I) is the dissociation curve of an amphoteric electrolyte. In the broad region of optimum p_H brightness very exactly \propto pigment concn. The decrease in fluorescence on the acid and alkaline side can be used as a measure of the no. of electrically neutral mols. (Zwitterions) and the dissociation const. of (I) can be thereby determined with min. amounts of material. Similar observations are recorded with lumilactoflavin (II). With the porphyrins a min. of fluorescence is observed in the isoelectric region. Phosphorescence of lactoflavin or (II) could not be observed.
H. W.

Flavin potentials. [Reduction-oxidation behaviour and a colour reaction of lactoflavin (vitamin-B₂). Flavins as biological hydrogen acceptors.] K. G. STERN (Ber., 1934, 67, [B],

654—655).—In reply to Kuhn *et al.* (this vol., 461) and Wagner-Jauregg *et al.* (A., 1933, 1183), it is pointed out that the normal potential of cryst. hepato- and extensively purified malto- and uro-flavin at p_H 7 is about -0.2 volt, whereas that of pyocyanine at p_H 7.0 is -0.034 volt. H. W.

Lyochrome from urine (uroflavin). W. KOSCHARA (Ber., 1934, 67, [B], 761—766).—Fresh urine is agitated with "Floridin XXF" (I) and the solid is treated with 40% $C_5H_5N-H_2O$. The pigments are adsorbed from the eluate by pptn. with $Pb(OAc)_2$ and treatment of the filtrate with H_2S . The eluates are reddish-brown and fluoresce strongly in ultra-violet light. Saturation with $(NH_4)_2SO_4$ causes the appearance of the colour of lyochrome, but further purification of the pigments is not effected by use of $COMe_2$ or salts of heavy metals. Their separation is effected chromatographically using (I) with $MeOH-H_2O-C_5H_5N$ as developer, the addition of a small amount of $AcOH$ to the latter being particularly advantageous. Thus is obtained uroflavin (II), $C_{18}H_{22}O_7N_4$, m.p. 272° (decomp.) when slowly heated. (II) is identical in cryst. form and lyochrome character with lactoflavin *d* (III), m.p. $267-268^\circ$. A mixture of (II) and (III) has m.p. $267-268^\circ$. No differentiation is observed when a mixture of (II) and (III) is examined chromatographically. The formulæ of (II) and (III) are not sufficiently well established to afford trustworthy evidence, but the pigments are considered to be non-identical. H. W.

Vitamin-C. XI. Efficacy of vitamin-C and the manner in which it is supplied. XII. Vitamin-C in the liver and adrenal glands of cattle. XIII. Extraction of vitamin-C and solvents. XIV. Extraction of vitamin-C and p_H of the solution. T. MATSUOKA (J. Agric. Chem. Soc. Japan, 1933, 9, 1117—1123), 1124—1129, 1130—1136, 1136—1140).—XI. Effective doses are reported. XII. Adrenals are richer in vitamin-C than liver. Cryst. hexuronic acid was isolated.

XIII. Cabbage juice was evaporated under reduced pressure and dried over H_2SO_4 . Vitamin-C is sol. in $EtOH$ and $COMe_2$, but insol. in Et_2O and light petroleum.

XIV. The p_H of the solution had no effect on the solubility of vitamin-C in $EtOH$ and $COMe_2$.

CH. ABS.

Chinese citrus fruits. III. Composition of juices of several species of Chinese oranges and tangerines, and their vitamin-C content. P. P. T. SAH, T. S. MA, V. HOO, and H. H. LEI (J. Chinese Chem. Soc., 1934, 2, 73—83).—Kwan Cheng, a Canton orange, is richest in ascorbic acid.

J. L. D.

Vitamin-C content of Chinese green and red peppers. P. P. T. SAH and H. C. CHANG (J. Chinese Chem. Soc., 1934, 2, 84—85).—Judged by I titration, *Capsicum annuum* (green fruit) contains no vitamin-C (I), but the red fruit is rich in (I). J. L. D.

Anti-pneumonia factor in fruits containing vitamin-C. H. VON EULER and M. MALMBERG (Naturwiss., 1934, 22, 205).—Lemon and red-currant juices contain a factor-I, not identical with ascorbic

acid, which aids recovery of guinea-pigs from pneumonia. R. K. C.

Significance of transpiration. H. F. CLEMENTS (Plant Physiol., 1934, 9, 165—172).—A discussion. A. G. P.

Chlorophyll production under various environmental conditions. G. B. ULVIN (Plant Physiol., 1934, 9, 59—81).—Leaves grown in continuous light contained more chlorophyll (I) per unit fresh or dry wt. or area than those grown in intermittent light. Maize plants showed markedly increased (I) formation following additions of 1 and 15 p.p.m. of Fe to the nutrient, but did not respond to addition of 1 p.p.m. of Mn. The % dry matter in leaves was directly proportional to the (I) content by wt. or area. Exposure to X-rays increased the amount of (I) in maize leaves. In sugar-cane receiving N as NO_3 , (I) production was $>$ that in plants supplied with NH_3-N . A. G. P.

Causes of colour change in blue-green algæ. M. C. SARGENT (Proc. Nat. Acad. Sci., 1934, 20, 251—254).—A high intensity of light and a low Fe content of the medium cause a decrease in the chlorophyll in *Glæocapsa montana*. No complementary chromatic adaptation was observed. H. G. R.

Oxygen consumption of *Chlorella pyrenoidosa* as a function of temperature and oxygen tension. P. S. TANG and C. S. FRENCH (Chinese J. Physiol., 1933, 7, 353—377).—The variation of the rate of O_2 consumption (A) with O_2 tension (P) follows the equation $A = P / (K_1 + K_2 P)$, where K_1 and K_2 are consts., the dependence of which on temp. is expressed by the equations of Arrhenius and van 't Hoff. The vals. of μ and ΔH (apparent heats of activation and reaction, respectively) between 8° and 20° are approx. the same (20,000 g.-cal.), but of opposite sign, that for μ being positive. A. L.

Oxidation processes in the needles of *Picea excelsa* in winter. T. M. ZACHAROVA (Biochem. Z., 1934, 270, 281—290).—The C content and heat of combustion of pine needles (I) are less for (I) kept in the dark or from the depth of a wood, than for those in the light. The malic acid content of the (I) of a darkened branch increases from Nov. to Jan., and of an undarkened branch from Nov. to March, the total amount found being greater in the light. The $H_2C_2O_4$ content of (I) of a darkened branch increases continuously, but of the undarkened branch does not increase. P. W. C.

Time relations in effect of ethylene chlorohydrin in increasing and of ethyl alcohol in decreasing the respiration of potato tubers. L. P. MILLER (Contr. Boyce Thompson Inst., 1934, 6, 123—128).—The increased CO_2 production (I) from potato tubers following exposure to vapour of CH_2Cl-CH_2-OH (II) commences approx. 12 hr. after treatment and the reduction of (I) by $EtOH$, approx. 2 hr. after treatment. (II) and $EtOH$ applied simultaneously or alternately tend to counteract each other's effects. A. G. P.

Respiration and catalase activity in *Saurum spadices*. A. W. H. VAN HERK and N. P. BADENHUIZEN (Proc. K. Akad. Wetensch. Amster-

dam, 1934, 37, 99—105).—The flower spikes of *S. guttatum* take up O₂ rapidly. The respiratory activity shows a broad optimum between p_H 6.6 and p_H 8, and is inhibited by the usual agents. Extracts show high catalase (I) activity (190—250 units per g.), which has an optimum val. at p_H 6.5—8 and is inhibited by HCN. The respiration of slices of tissue is accelerated by addition of (I), and the possible correlation of the two activities is discussed.

R. K. C.

Oxidase system of a non-browning yellow peach. Z. I. KERTESZ (New York State Agric. Exp. Sta. Tech. Bull., 1933, No. 219, 14 pp.).—Lack of discoloration in peach is not due to low activity of oxidising enzymes, but to deficiency or absence of pyrocatechol-tannin compounds which form an essential component of the oxidising system. A. G. P.

Determination of peroxidase activity. D. A. PACK (Ind. Eng. Chem. [Anal.], 1934, 6, 170—171).—The peroxidase activity of fruit juices is much greater if obtained by grinding with fine sand in H₂O or the buffer solution than by pressing, and if measured at the optimum p_H than at p_H 4.5. The p_H optimum for pears is 6.2, and for strawberries, cauliflowers, asparagus, and potatoes between 6 and 7.

R. S. C.

Formation of cellulose membranes by microscopic particles of uniform size in linear arrangement. W. K. FARR and S. E. ECKERSON (Contr. Boyce Thompson Inst., 1934, 6, 189—203).—Fibrils of cell membranes from a no. of plants consist of particles of cellulose with a pectic covering arranged in a linear manner. A. G. P.

Red and brown algæ. T. DILLON and T. O TUAMA (Nature, 1934, 133, 837; cf. this vol., 571).—Cellulose has been obtained from *Laminaria* and converted into a sugar which gave phenylglucosazone but no insol. phenylhydrazone. L. S. T.

Acetyl and methoxyl content of pine-wood. E. HÄGGLUND and O. SANDELIN (Svensk Kem. Tidskr., 1934, 46, 83—87).—Pine-wood (I) freed from lignin (II) by repeated treatment with Cl₂ and extraction with COMe₂-C₅H₅N contained 0.80% OMe, OEt being probably absent. The OMe content of (I) is not wholly attributable to (II), but about one eighth is associated with the 70% of carbohydrate (III). Of the Ac groups in (I), at least 60% are attached to (III). W. O. K.

Transformation of the methoxyl group in lignin in the process of decomposition of organic residues by micro-organisms. S. A. WAKSMAN and H. W. SMITH (J. Amer. Chem. Soc., 1934, 56, 1225—1229).—Growth of *Agaricus campestris* on fresh or composted [which results in an increase of the amount of lignin (I) present] horse manure causes a decrease in the amount of (I); the OMe content of the residual (I) is not appreciably altered, but the mol. is considerably modified. Prolonged decomp. of plant residues under aerobic and anaerobic conditions leads to an increase in (I); the OMe content of the residual acid-(I) is considerably reduced (especially in the latter case). Peat formation (decomp. of plant material under anaerobic conditions) is accompanied

by an accumulation of (I) and a decrease in OMe content [which characterises the gradual transformation of (I) into dark-coloured humus substances]. Sphagnum plants contain little OMe, but much uronic acid (II) (which is resistant to decomp.); anaerobic decomp. gives a type of peat which is rich in lignin-like complexes of low OMe and high (II) content.

H. B.

Formation of aromatic substances and terpenes in plants. T. WEEVERS (Pharm. Weekblad, 1934, 71, 621—630).—The formation of terpenes (I) in the plant is parallel with the formation of lignin. (I) may occur in certain plants as a result of pathological conditions, which bring about degeneration of the cells. S. G.

Determination of pentosans in vegetable materials containing tannin. A. P. SAKOSTSCHIKOFF, W. I. IWANOWA, and A. M. KURENOWA (Ind. Eng. Chem. [Anal.], 1934, 6, 205—208).—Determination of pentosan (I) in cotton-seed hulls (II) by Tollens' method gives low results, the error increasing with increasing tannin content of (II). The real (I) is found by addition of the results obtained (i) on the aq. extract of (II) (after removal of tannins from the solution), (ii) on an acid extract of the residue from (i), and (iii) on the solid residue from (ii).

R. S. C.

Carbohydrates of the bulb of *Narcissus tazetta*, L., var. *chinensis*, Roem. UI. **Enzymic hydrolysis of glucomannan.** Y. KIHARA (J. Agric. Chem. Soc. Japan, 1933, 9, 770—772).—When kept with *Eulota* extract for 3 days, glucomannan solution rapidly decreased in viscosity, affording a substance, m.p. 183° (decomp.), $[\alpha]_D^{25} +47.26^\circ$ (Ac derivative, m.p. 137°), which is not pptd. by Ba(OH)₂ or Pb(OAc)₂ and is hydrolysed by maltase but not by emulsin.

CH. ABS.

Methods of determining starch in plant tissues. F. E. DENNY (Contr. Boyce Thompson Inst., 1934, 6, 129—146).—To ensure conversion of potato-starch (I) completely into glucose by taka-diaxase (II) a suitable ratio of (II) : (I) must be used, p_H 3.0—5.0 must be maintained, and approx. 4 hr. contact allowed. Solutions of (II), free from reducing substances, of high amyolytic power and stable at room temp. for several weeks, may be obtained after dialysis in collodion sacs. Preliminary heating of (I) to 80° is sufficient to permit complete hydrolysis by (II). Determinations of (I) in the various organs of a no. of plants are recorded. Vals. of (I) obtained by the direct action of (II) on powdered plant tissue are > those resulting from extraction of (I) by CaCl₂, pptn. as the I-compound, removal of I and Ca, and treatment of the residue with (II). Decomp. of non-starchy substances in the former method is probable. The destruction of sugar under conditions required for the hydrolysis of starch does not occur unless the proportion of acid used is > twice the customary amount. A. G. P.

Determination of biologically important sugars in the presence of non-sugar reducing substances. O. LEHMANN (Diss., Leipzig, 1931; Bied. Zentr., 1934, A, 4, 364—365).—The Hagedorn-Jensen method is adapted to the determination of plant

sugars. Fermentation methods are utilised to separate hexoses from pentoses (the latter being determined by the furfuraldehyde method) and reducing sugars from non-sugar reducing substance in H_2O or Et_2O extracts of plant tissues. A. G. P.

Determination of coumarin in plant material. I. J. DUNCAN and R. B. DUSTMAN (Ind. Eng. Chem. [Anal.], 1934, 6, 210—213).—Coumarin (I) is only slowly removed (completely in 120 hr.) by extraction (Soxhlet) of sweet clover (II) with Et_2O . Long heating of the solution, however, destroys some (I). The (I) content of (II) is determined by repeated distillation with steam in vac., removal of tannins etc. from the distillate by $Pb(OAc)_2$, and titration with $KMnO_4$. For comparative purposes four distillations suffice and the Pb treatment may be omitted. R. S. C.

Colour reaction of chrysanthemum-monocarboxylic acid (hydrolysis product of pyrethrin I) and its detection in the urine excreted after administration of pyrethrins. M. AUDIFFREN (J. Pharm. Chim., 1934, [viii], 19, 535—536).—Chrysanthemum-monocarboxylic acid solution (1 c.c.), Denigès reagent (1 c.c.), and conc. H_2SO_4 (0.4—0.5 c.c., added rapidly without mixing) when mixed give an immediate red or rose changing to violet and green and a yellow ppt. after 24 hr. (sensitivity 1 : 100,000). The first fractions of the distillate from the urine of patients treated with pyrethrins give the reaction. E. H. S.

Determination of the acids of plant tissue. III. **Determination of citric acid.** G. W. PUCHER, H. B. VICKERY, and C. S. LEAVENWORTH (Ind. Eng. Chem. [Anal.], 1934, 6, 190—193; cf. this vol., 572).—1—20 mg. of citric acid (I) is determined within $\pm 5\%$ by oxidation to $CHBr_2 \cdot CO \cdot CBr_3$ (II), debromination of the latter in light petroleum with aq. Na_2S , and titration of the liberated NaBr. Conversion of (I) into (II) is regularly about 90% under the conditions described. R. S. C.

Localisation of fatty oils and starch in cells of cultivated beet. S. KOPUL-GOMOLYAKO (Nauk. Zapiski Tzuk. Prom., 1933, 10, No. 33, 91—100).—Differences in fat content between individual groups are not as great as among separate plants of the same group. The significance of the fatty oils is discussed. Starch is found only in the mangold group. CH. ABS.

Constituents of tobacco. III. **Colouring matters of the flower.** I. K. YAMAFUJI (J. Agric. Chem. Soc. Japan, 1933, 9, 797—802).— $MeOH-HCl$ afforded an anthocyan (insol. picrate) affording an anthocyanidin and a monosaccharide. The residue, mixed with $CaCO_3$ and extracted with hot $EtOH$, afforded a flavone. CH. ABS.

Gradient composition of rose shoots from tip to base. H. B. TUKEY and E. L. GREEN (Plant Physiol., 1934, 9, 157—163).—In 100-cm. shoots there was a rising gradient of H_2O , ash (I), and total N (II) and a falling gradient of starch (III) from base to tip. Shoots grown in high-N nutrients had more (I) and (II) and less (III) throughout their lengths than did those grown with less N. The distribution of starch in various stem tissues is examined. A. G. P.

Two saponins from soya beans. K. OKAMO and I. OHARA (J. Agric. Chem. Soc. Japan, 1933, 9, 1249—1258).—Sumiki's cryst. saponin (I), $C_{48-50}H_{77-81}O_{18}$, m.p. 225—227°, and an amorphous saponin (II), $C_{45-51}H_{79-83}O_{19}$, m.p. 216—218°, were obtained. On hydrolysis (I) affords a sapogenin, $C_{30-32}H_{48-52}O_8$, glycuronic acid (III), galactose (IV), and rhamnose (V); (II) affords a sapogenin, $C_{31-33}H_{50-54}O_8$, and (III), (IV), and (V). Five saponin isomerides, m.p. 201°, 235°, 239°, 260°, and 248—249°, were isolated according to the duration of hydrolysis. When heated with CuO or $PbCrO_4$, the saponins and sapogenins afford CH_4 and C_2H_6 . The saponins have no hæmolytic power. CH. ABS.

[Constituents of] *Ceanothus velutinus*. L. W. RICHARDS and E. V. LYNN (J. Amer. Pharm. Assoc., 1934, 28, 332—336).—The leaves of *C. velutinus* furnish 0.14—1.21% of an oil which consists chiefly of Et and cinnamyl cinnamates, together with salicylaldehyde, terpenes, and esters of an unidentified alcohol (diphenylurethane, m.p. 56°; phthalate, m.p. 204—205°) with cinnamic and probably valeric acids. The root bark furnishes 0.1% of an alkaloid, $C_{23}H_{28}O_4N_2$, m.p. 270° (decomp.) (unstable hydrochloride, decomp. 240°). The symptoms of a dermatitis caused by the leaves are described. A. E. O.

Constituents of native (Austrian) herbs. IV. J. ZELLNER (Arch. Pharm., 1934, 272, 601—607; cf. A., 1927, 598).—The rhizomes of *Petasites officinalis*, Moench, contain 2.5% of resins and small amounts of KCl, invert sugar (I), choline, terpenes, and a mixture (II), m.p. 132°, of sterols. Dry leaves of *Globularia nudicaulis*, L., contain ceryl alcohol (mainly in the fatty covering), (I), a mixture probably of stearic and palmitic acids, resin acids, lecithin, ? free choline, tannins, BzOH, a glucoside (? aucubin), possibly globularin, mannitol, (II), and a pectin-like carbohydrate. R. S. C.

Chemical composition of *Daphne genkwa*. M. NAKAO and K. F. TSENG (J. Shanghai Sci. Inst., 1933, 1, 1—15).—BzOH, sitosterol, apigenin, m.p. 352° (Ac derivative of Me_2 ether, m.p. 199—200°), and a flavone, *genkwain*, $C_{16}H_{12}O_5$ (I), m.p. 286° (Ac derivative, m.p. 196°; Bz derivative, m.p. 207°) were isolated from the flowers of *D. genkwa*, Sieb et Zucc. (I) with CH_2N_2 gives apigenin Me_3 ether, contains 1 OMe, and is not identical with acacetin. Fusion with KOH gives phloroglucinol and $p-OH \cdot C_6H_4 \cdot CO_2H$, whilst with 50% KOH $p-C_6H_4 \cdot Ac \cdot OH$ and phloroglucinol Me_1 ether are also obtained. (I) is therefore considered to be 4' : 5-dihydroxy-7-methoxyflavone. A. A. L.

Constituents of be-still nuts, *Thevetia Neriiifolia*. K. K. CHEN and A. L. CHEN (J. Biol. Chem., 1934, 105, 231—240).— Et_2O extraction of the kernels of the nuts yields a fatty oil containing a *phytosterolin*, $C_{17}H_{35}O \cdot C_6H_{11}O_5$, m.p. 291—292.5° (corr., charring). $MeOH$ extraction of the defatted residue yields a mixture containing the following glucosides: *ahouain*, $C_{10}H_{18}$ or $^{20}O_{10}$, softens at 94—95°, foams at 112°, m.p. 185° (decomp.); *kokilphin*, $C_{33}H_{63}$ or $^{62}O_{30}$, m.p. 188.5—189° (corr.); *thetevin* (I), $C_{29}H_{46}O_{13} \cdot 2H_2O$,

m.p. 193° (corr.), $[\alpha]_D^{25}$ -62.5° in MeOH. The digitalis-like action of (I) is $\frac{1}{7}$ — $\frac{1}{8}$ that of ouabain.

A. E. O.

Soluble solids in the water-melon. L. R. TUCKER (Plant Physiol., 1934, 9, 181—182).—Refractometric observations of the distribution of sol. solids are recorded.

A. G. P.

Arsenic content of *Chondrus*. C. H. LA WALL and J. W. E. HARRISON (J. Amer. Pharm. Assoc., 1934, 23, 308—309).—Genuine unbleached or sun-bleached *Chondrus* contains As naturally, and its As content is > the tolerance for As in food products.

A. E. O.

Variation in the phosphorus content of maize meal used in rachitogenic diets. W. L. DAVIES (Analyst, 1934, 59, 340—341).—The % of H₂O, ash, and P in 9 samples of maize (I) are given, and the ratios 100P : ash and Ca : P (II) are calc. (II) varies from 2.8 to 4.8, indicating that analysis of (I) used in making up diets is necessary.

E. C. S.

Diurnal periodicity of mineral nutrition [in plants]. N. POTAPOV and N. J. STANKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 40—45).—Absorption of NO₃' and PO₄' by Indian corn (horse's tooth), kept without the sp. salt for 2 days prior to the test, in H₂O culture, increases rapidly after sunset and reaches a max. at night at a period coincident with that of greatest respiration intensity (by determination of H₂CO₃ in the medium), and decreases considerably during the day. The respiratory energy of the root cells is the main factor in the absorption of electrolytes.

J. W. B.

Influence of salts on development and sugar content of water-melons. I. D. ZNAMENSKI (Bull. Appl. Bot. Leningrad, 23, 297—319; Bied. Zentr., 1934, A, 4, 453).—Small additions of Na₂SO₄ or NaCl stimulated the growth of water-melons in pot cultures, Na₂SO₄ producing an increase in sugar content (notably fructose).

A. G. P.

Elements of mineral nutrition as factors changing the drought-resistance of plants. N. L. UDOLSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 45—48).—Addition of Na₂HPO₄ fertiliser (I) [+Ca(NO₃)₂] in dry soil (black earth) increases the H₂O-retaining capacity of the plasma, greatest receptivity to (I) being shown by *Pseudo-hostianum* 0303, of which the H₂O balance (at a subnormal level) and H₂O assimilation during drought are maintained by (I), no decrease in H₂O content during the hot hr. being observed. Conversely the yield of *Cærulescens* 04972 was decreased in all experiments with fertilisers.

J. W. B.

Replacement of potassium by rubidium in *Nitzschia closterium*. F. A. STANBURY (J. Marine Biol. Assoc., 1934, 19, 931—937).—In this marine diatom Rb can partly but not entirely replace K. The ratio of P requirement to K requirement is 50 : 1.

L. D. G.

Classification of the chemical elements with respect to their functions in plant nutrition. R. W. THATCHER (Science, 1934, 79, 463—466; cf. A., 1933, 101).—An attempt to correlate known or possible functions of the different elements in plant

nutrition with their general chemical properties. The groups proposed and discussed are: (I) H and O, energy exchange elements; (II) C, N, S, and P, energy storers; (III) Na, K, Ca, and Mg, translocation regulators; (IV) Mn, Fe (Co, Ni), Cu, and Zn, oxidation-reduction regulators; (V) B, Al, Si, As, Se; (VI) Cl, F (Br and I); (VII) Co and Ni; (VIII) Ge, Ga, and other rare elements.

L. S. T.

Factors affecting assimilation of ammonium- and nitrate-nitrogen particularly in tomato and apple. V. A. TIEDJENS (Plant Physiol., 1934, 9, 31—57; cf. B., 1933, 981).—Optimum assimilation of NO₃' by tomato and apple followed absorption from media having p_H 4.0. The corresponding optimum for NH₄' was p_H 5.0—6.5. Plants absorbed NH₄' unchanged, and protein synthesis continued immediately and more rapidly than when NO₃' was supplied. Direct relationships exist between the [NO₃'] of the medium and the growth produced, provided the reductase of the plant remains fully active. The [NH₄-N] necessary to produce a given growth was < the [NO₃-N]. Plants containing much available carbohydrate assimilated NH₄' the more readily. Feeding with NH₄-N resulted in the formation of more sol. org. N (I) in the plant than when an equal concn. of NO₃-N was used. (I) is directly correlated with [NH₄-N] in the medium. When both forms of N are present the relative rates of absorption are partly dependent on the p_H of the medium.

A. G. P.

Influence of hydrogen-ion concentration of the culture solution on absorption and assimilation of nitrate- and ammonium-nitrogen by peach trees grown in sand cultures. O. W. DAVIDSON and J. W. SHIVE (Soil Sci., 1934, 37, 357—385).—The rates of intake of N from solutions containing NH₄' or NO₃' as sole source of N are compared. Better growth occurred in NH₄' media at p_H 6 than at p_H 4 or 8, and in NO₃' media at p_H 4 than at p_H 6 or 8. NH₄' at p_H 6 and NO₃' at p_H 4 produced approx. the same effects. The rate of intake of N in each form followed the order of growth differences, but at favourable p_H NH₄'-N was absorbed more rapidly than NO₃'-N. Assimilation of NH₄' commenced in the roots (I) and reduction of NO₃' was almost completed in (I). Healthy growth and high production of plant-tissue are associated with low protein-N and high amide-, NH₂-, and humin-N in both stems (II) and (I), whereas basic N is low in (II) and high in (I).

A. G. P.

Influence of temperature on the physiological reaction of ammonium nitrate. P. STREBEYKO (Polish Agric. Forestal Ann., 1932, 28, 357—370).—The reaction (NH₄ : NO₃ taken up simultaneously by maize in H₂O cultures) is affected by p_H and temp. The higher is the temp. the greater is the amount of NO₃' absorbed, whilst the amount of NH₄' is const.

CH. ABS.

Nitrogen distribution in the leaf-proteins of Chinese cabbage during growth. H. C. KAO (Chinese J. Physiol., 1933, 7, 379—386).—The N content of the green leaves, the roots and stems, and the stalk decreases in this order, the vals. decreasing with age. Two protein fractions are prepared from the

leaves, one by coagulation of the expressed juice and the other by extraction of the pulp residue with aq. NaOH and pptn. with AcOH, and their N distribution is determined for different stages of growth.

A. L.

Isotopic fractionation of water by physiological processes. E. R. SMITH (Science, 1934, 79, 454—455; cf. this vol., 570).

L. S. T.

Isotopic carbon dioxide and oxygen in plants? A. MOLDAVAN (Science, 1934, 79, 455).—CO₂ absorbed during photosynthesis (I) and O₂ absorbed during respiration (II) may differ isotopically from the O₂ rejected during (I) and the CO₂ rejected during (II).

L. S. T.

Hydrogen-ion concentration in relation to growth and ripening in fruits. J. S. CALDWELL (U.S. Dept. Agric. Tech. Bull., 1934, No. 403, 53 pp.).—In many fleshy fruits examined, the *p_H*, immediately after setting, remains high for a short period, corresponding with the stage of rapid cell division. Total solids are high at this stage. Subsequently there is a rapid increase in acidity and a heavy intake of H₂O, the period of max. active acidity coinciding with that of max. hydration of the fruit, and with a marked flattening in the growth (wt.) curve. Towards maturity acid production and H₂O content decline. Changes in H₂O absorption by the hydrophilic colloids of the fruit are probably controlled by the [H⁺] of the tissue fluids.

A. G. P.

Relation of "dark centre" to the composition of rutabagas. E. B. HOLLAND and C. P. JONES (J. Agric. Res., 1934, 48, 377—378).—The appearance of "dark centre" in roots is associated with a decreased % of carbohydrate which is partly replaced by pentosans and galactan.

A. G. P.

Plant injury caused by vapours of mercury and compounds of mercury. P. W. ZIMMERMANN and W. CROCKER (Contr. Boyce Thompson Inst., 1934, 6, 167—187).—Vapour containing Hg emanating from soil treated with various org. and inorg. Hg compounds injured many varieties of plants in the same greenhouse. In general the extent of the injury varied with the v.p. of Hg at any particular temp. Metallic Hg was detected in the air surrounding treated soil and also in leaves of plants enclosed in glass cases with a small amount of soil treated with HgCl₂.

A. G. P.

Effects of radiation from a quartz-mercury-vapour lamp on the mineral composition of plants. W. D. STEWART and J. M. ARTHUR (Contr. Boyce Thompson Inst., 1934, 6, 225—245).—Irradiation (I) increased the ash, Ca, and/or P content of soil-grown plants in relatively low but not in high light intensity. In 48—72 hr. after brief treatment (15—120 sec.) the above effects occurred in leaves, but stems showed a decline in ash and an increase in P. With prolonged treatment the general effect was apparent in both leaves and stems. Plants grown in sand-culture, with nutrients differing considerably from those in soil, were more sensitive to injury by (I), which caused changes in ash content even in plants grown in high light intensity. (I) had no

influence on the Mn or Mg of plants. The effective wave-lengths of ultra-violet light used were those inducing antirachitic effects and the activation of ergosterol. Cabbage, having no anti-rachitic effects even after (I), was not affected in mineral content by (I). Irradiated ergosterol in olive oil applied to the basal leaves of plants produced in them an increase in ash content.

A. G. P.

Effect of soft X-rays on germination of wheat seeds. H. M. BENEDICT and H. KERSTEN (Plant Physiol., 1934, 9, 173—178).—Brief irradiation resulted in increased diastatic activity and sugar content, both of which declined with prolonged treatment. Irradiated seeds probably cannot take in H₂O or utilise their additional sugar as readily as untreated controls.

A. G. P.

Virucidal action of high-frequency sound radiation. W. N. TAKAHASHI and R. J. CHRISTENSEN (Science, 1934, 79, 415—416).—Tobacco mosaic virus (I) is inactivated by high-frequency sound radiation. 2 hr. exposure to a frequency of 450,000 cycles per sec. inactivates (I) towards *Nicotiana glutinosa*.

L. S. T.

Plant immunity. K. T. SUCHORUKOV, E. GERBER, G. BARABANOVA, and N. BORODULINA (Sci. Mem. Univ. Saratov, 1933, 10, 106—118).—The reducing sugar and peroxidase content of cabbage leaves or juice infected with *Botrytis cinerea* (I) are <, and the catalase and NH₃ content are >, for healthy plants. (I) produces a sol. substance toxic to plant cells. No definite relationships are found between immunity to *Sclerotinia libertiana* and composition of carrot roots. *Fusarium nivium* does not possess proteolytic enzymes.

R. T.

Standardisation of biological products. P. BRUÈRE (Bull. Soc. Chim. biol., 1934, 16, 156—159).

A. L.

Improved gas analysis. R. MARGARIA (Biochem. Z., 1934, 270, 444—447).—A modification of the usual apparatus is described, the dead space between the CO₂- and O₂-absorption pipettes being eliminated.

P. W. C.

Determination of cholesterol. II. Volumetric and gravimetric methods. A. S. RUIZ and I. TORRES (Anal. Fis. Quim., 1933, 31, 686—694; cf. A., 1933, 1063).—The gravimetric method of Szent-Györgyi is preferred (blood-cholesterol, average 144 mg. per 100 c.c.; recovery 100.2%). The volumetric method of Okey as modified by Turner is satisfactory, particularly for plant extracts. Bang's method gives a low recovery (66%) and is applicable only when neutral fats are simultaneously determined.

R. K. C.

Permanganate oxidation in the determination of iodine. B. GRODK (Biochem. Z., 1934, 270, 291—296).—A method is described whereby small amounts of I obtained by ashing org. material and extracting can be determined by Na₂S₂O₃ titration after oxidation with KMnO₄ to IO₃⁻; the excess of KMnO₄ being destroyed with NaNO₂ and of NaNO₂ with urea. The error with 1—2 × 10⁻⁶ g. of I is < ±4%.

P. W. C.