BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JULY, 1936.

General, Physical, and Inorganic Chemistry.

Intensity anomalies in the Lyman series of hydrogen. T. Takamine and T. Suga (Nature, 1936, **137**, 827—828). L. S. T.

Oxygen in solar prominences. A. L. Narayan and T. Royds (Current Sci., 1936, **4**, 734).—The O_2 triplet at λ 7770 A. has been observed in a prominence at a height of 9000 miles above the chromosphere. L. J. J.

Zeeman and Paschen–Back effects in the case of extreme *j–j* coupling. $2p^5ns$ configurations of neon. P. Jacquinot (Compt. rend., 1936, **202**, 1578—1580). H. J. E.

Induced predissociation in the absorption spectrum of sulphur. V. Kondrateev and E. Olsson (Z. Physik, 1936, **99**, 671—676).—The energy of dissociation of the normal state of S_2 is $\not> 4{\cdot}1$ volts. A. B. D. C.

Intensity distribution in the diffuse series of potassium. P. A. Coenen and H. A. Kramers (Physica, 1936, **3**, 341—345).—Quantum-mechanical calculation of the intensities of the diffuse series of K is in accord with experiment (this vol., 261) and explains the anomaly of the exceptional weakness of the second line. J. W. S.

Colour phenomenon in " colloidal " potassium vapour. J. Kunz (Physikal. Z., 1936, **37**, 415).—H_2 is passed over molten K in an evacuated tube. On placing the tube in connexion with another exhausted tube an intense but short-lived colour appears in the second tube. The colour varies along the tube. The pptd. K is strongly photo-electric. A. J. M.

Lines in the arc spectrum of cobalt not emitted by Co I. M. T. Antunes and M. A. Catalán (Anal. Fís. Quím., 1935, **33**, 391—432).—A crit. examination is made of the lines between 2449 and 19,778 A. attributed to Co, and a list of the respective levels, but omitting lines emitted by Co I, is given. F. R. G.

Structure of the spectrum of unexcited cobalt. M. A. Catalán and M. T. Antunes (Anal. Fís. Quím., 1936, **34**, 207—297).—For Co I, λ and ν with emission and absorption intensities and levels are tabulated for the range 2012—18,273 A. A supplement to the list of lines not emitted by Co I (see above) is also given. F. R. G.

Electrical quadrupole moment and magnetic moment of $^{63}_{29}Cu$ and $^{65}_{29}Cu$. H. Schüler and T. Schmidt (Z. Physik, 1936, **100**, 113—116).—The quadrupole moment of the two isotopes is $\sim -0{\cdot}1 \times 10^{-24}$, and the magnetic moments are 2·5 and 2·6 for 63 and 65, respectively. A. B. D. C.

Absorption spectrum of rubidium. N. T. Zé and W. W. Po (Compt. rend., 1936, **202**, 1428—1430).—A no. of new lines, observed at 350—550°, are recorded. L. J. J.

Transmission and reflexion of thin silver layers in the infra-red and ultra-violet. F. Goos (Z. Physik, 1936, **100**, 95—112).—Transmission and reflexion data are given for Ag layers 0·8—142 mμ thick on quartz from 1050 to 265 mμ. A. B. D. C.

Spectra of xenon in the extreme ultra-violet. J. C. Boyce (Physical Rev., 1936, [ii], **49**, 730—732).—Using increased dispersion and resolving power, revised and extended data and classifications are tabulated for Xe I, II, III in the range λλ 2000—600. N. M. B.

Absorption spectrum of hydrogen. III. Auto-ionisation in the term $3p\pi\,^1\Pi_u$ of H_2 and its selection rules. Ionisation energy of H_2. H. Beutler and H. O. Jünger (Z. Physik, 1936, **100**, 80—94; cf. this vol., 261).—The ionisation energy of H_2 is 124,429 ± 13 cm.$^{-1}$ A. B. D. C.

Reversal temperature and population of excited states in the cæsium discharge. F. L. Mohler (J. Res. Nat. Bur. Stand., 1936, **16**, 227—231).—Data are recorded for the lines $6S-nP$ ($n=6-11$) at a no. of pressure and current vals. L. J. J.

Analytical and quantitative lines of hafnium in the arc spectrum. S. Piña de Rubies and J. G. Aguado (Anal. Fís. Quím., 1935, **33**, 549—565).—The method previously described (A., 1934, 48) is applied to Hf. A list of Hf lines and of those lines of other elements which might be mistaken for the principal Hf lines, is given. F. R. G.

Quartz mercury arc. A. J. Allen (Science, 1936, **83**, 336). L. S. T.

Fluorescent emission of the mercury line 2537 A. at pressures between 10^{-3} and 10^{-1} mm. P. Pringsheim and O. D. Saltmarsh (Proc. Roy. Soc., 1936, **A**, **154**, 90—95).—The degree of polarisation of the fluorescence radiation of Hg has been measured. The phenomena are analogous to those observed with Na vapour. It is considered that the observed fluorescence is due, not to Hg atoms, but to van der Waals mols. L. L. B.

Electrical quadrupole moment of the $^{209}_{83}Bi$ nucleus. H. Schüler and T. Schmidt (Z. Physik, 1936, **99**, 717—728).—This quadrupole moment is $-0{\cdot}4\times10^{-24}$. A. B. D. C.

Scale of wave-lengths in the infra-red solar spectrum. H. D. Babcock, C. E. Moore, and W. P. Hoge (Astrophys. J., 1936, 83, 103—120). L. S. T.

Ultra-violet spectrum of the night sky. A. Arnulf (Compt. rend., 1936, **202**, 1412—1414).—Data are recorded for λλ 3556—2979 A. L. J. J.

Enhancement of red lines and bands in the auroral spectrum from a sunlit atmosphere. L. Vegard and E. Tønsberg (Nature, 1936, 137, 778—779).—Sunlight produces a pronounced enhancement of certain bands of the first positive group of N_2, and of the red line 6300 A., which is due probably to production of O_3 by the sun's radiation. L. S. T.

Colour temperatures and continuous absorption of hydrogen for stars of the first spectral types. A. Arnulf, D. Barbier, D. Chalonge, and (Mlle.) R. Canavaggia (Compt. rend., 1936, 202, 1571—1573). H. J. E.

Search for the bands of boron compounds in stellar spectra. P. Swings (Astrophys. J., 1936, 83, 177—178).—BH bands in late-type stars could not be detected. L. S. T.

Spectrum of Arcturus. S. G. Hacker (Astrophys. J., 1936, 83, 140—161).—At. and mol. spectra identified in the region 4119—6743 A. are summarised. L. S. T.

Resonance phenomena in ionised gases. W. Sigrist (Helv. phys. Acta, 1935, 8, 317—320; Chem. Zentr., 1935, ii, 1316—1317). H. J. E.

Sparks between flame electrodes. M. Pierucci (Nuovo Cim., 1935, [ii], 12, 240—242; Chem. Zentr., 1935, ii, 1317).—A spark discharge between two Bunsen coal-gas flames, inclined towards one another so as to serve as electrodes, has been investigated, using plain gas flames and flames charged with salt solutions from an atomiser. In general at. but not ionic spectra are emitted. J. S. A.

Investigation of electrical discharges in gases with the cloud chamber. E. Flegler and H. Raether (Z. Physik, 1936, 99, 635—642).—Study of initiation of self-maintained discharges shows that photo-ionisation, rather than space charge, gives the necessary initial conditions. A. B. D. C.

Increase of sparking potential by irradiation with ultra-violet light. W. Seitz and W. Fucks (Naturwiss., 1936, 24, 346).—Contrary to expectation, for certain cathodes (*e.g.*, Ag) and gases (*e.g.*, A) at moderate pressures, an increase in the sparking potential was observed when the cathode was irradiated with ultra-violet light. For a Zn cathode and A, however, the potential decreased. A. J. M.

Spectral investigation of the thread ray discharge. W. Hanle and W. Nöller (Physikal. Z., 1936, 37, 412—414).—The spectrum of the thread ray and its surrounding radiation has been investigated, and the electron velocity distribution in both radiations is obtained from a study of intensities in the line spectra. The methods of excitation are discussed, and the effect of an electric field on the radiation is examined. A. J. M.

Fine structure of the L_{23} absorption edge of magnesium metal. H. W. B. Skinner and J. E. Johnston (Nature, 1936, **137**, 826—827). L. S. T.

Absorption of soft *X*-rays in aluminium. G. B. Bandopadhyaya and A. T. Maitra (Phil. Mag., 1936, [vii], 21, 869—880).—The mass absorption coeff. of Al was measured for λλ 7—24 A. H. J. E.

Atomic scattering factor of cadmium for Cu $K\alpha$ radiation. G. W. Brindley (Proc. Leeds Phil. Soc., 1936, 3, 200—207).—The intensities of reflexion of Cu $K\alpha$ radiation from finely divided Cd have been measured and compared with those of Al, the at. scattering factor of the Cd atom at room temp. being deduced. The irregularities when plotted against $\sin\theta/\lambda$, similar to those found with Zn, indicate that in Cd the atoms have a greater mean amplitude of vibration parallel to the *c* axis than in the basal plane. J. W. S.

Atomic scattering factor of zinc. C. M. Kotin and J. Losada (Anal. Fís. Quím., 1935, 33, 597—601).—The scattering curve for Zn has been obtained by the Debye–Scherrer method, and is comparable with the theoretical curve of James *et al.* (cf. A., 1931, 889). F. R. G.

Screening doublets of *X*-ray spectra. A. E. Sandström (Z. Physik, 1936, 99, 622—625). A. B. D. C.

Constant *A* in Richardson's equation. E. Wigner (Physical Rev., 1936, [ii], 49, 696—700).—The chemical const. of the electron gas in the high-temp. region, where all measurements are made, is different from its val. at very low temp. (cf. Herzfeld, A., 1930, 391). The high-temp. val. of the Richardson const. *A*, which thus differs from the low-temp. val., is calc. in terms of thermodynamic quantities. N. M. B.

Theory of the work function. II. Surface double layer. J. Bardeen (Physical Rev., 1936, [ii], 49, 653—663; cf. A., 1935, 1050).—In order to determine the moment of the electrostatic surface double layer, the electronic surface charge density is calc. For Na, the vals. for the work function and moment of the double layer are 2·35 and 0·4 e.v. (including the effect of polarisation forces), and 2·0 and 1·0 e.v. (omitting these forces), respectively. N. M. B.

Photo-electric properties of sodium films on aluminium. J. J. Brady and V. P. Jacobsmeyer (Physical Rev., 1936, [ii], 49, 670—675; cf. A., 1932, 1184).—The max. sensitivity of Na films on Al was not attained for a film thickness of <80 mol. layers; it then remained const. for greater thicknesses. No detectable photo-current was observed for <5 mol. layers. Spectral distribution curves, analysed according to Fowler's theory, indicate a const. val. of 5150 A. for the threshold of the Na film for all film thicknesses. Current–voltage curves for different thicknesses, analysed according to Du Bridge's theory, indicate that the work function of the various films is the same, the val. for the freshly distilled Al on which the deposits were made being 4·08 volts, which gives the val. 3020 A. for the threshold of Al. The photo-electric current showed a decrease, probably due to surface migration of the Na atoms in forming aggregates, immediately after forming a film, but the decrease was much less for films > 50 mol. layers. N. M. B.

Temperature of electrons (T_e) in the positive column of a discharge in a mixture (Ne–Na). W. Uyterhoeven and C. Verburg (Compt. rend., 1936, **202**, 1498—1500; cf. A., 1935, 1438).—The positive ionic current collected near the walls is a max. when the wall temp. is 260°. T_e ($1T_e = 13{,}200°$ abs.) is a max. at 240°, *i.e.*, when there is 0·01 Na ion for 100 Ne, but decreases towards the centre of the tube. The increase in potential gradient is attributed to the presence of easily ionisable Na. R. S.

Influence of metastable atoms on the electron temperature in the positive column. G. Spiwak and E. Reichrudel (Physica, 1936, **3**, 301—306).—At high c.d. and with large concns. of impurity, ionisation of the gases and impurities by collision with electrons plays the principal part in controlling electron temp., but with low c.d. and with small concns. of impurity metastable atoms have a considerable influence. J. W. S.

Cæsium–oxygen films on tungsten. J. H. Lees (Phil. Mag., 1936, [vii], **21**, 1131—1139; cf. A., 1925, ii, 254).—Max. emission from Cs-coated W filaments at 780° abs. is observed after treatment with O_2 at relatively high pressure, followed by momentary heating to 1800° abs. The emission is decreased by activation above 2000° abs., owing to evaporation of the activated O. The adsorption of O_2 reaches equilibrium rapidly. Some evidence is obtained that O_2 penetrates the W lattice. J. W. S.

Method of measuring secondary-electron emission from filaments. L. R. G. Treloar (Proc. Physical Soc., 1936, **48**, 488—497).—An indirect method is described, and gives results for W and Ta filaments in agreement with available data. N. M. B.

Electron energies and excitation in the helium positive column. F. L. Jones (Proc. Physical Soc., 1936, **48**, 513—526).—A distribution function is suggested to account for available data on the intensities of lines emitted from He discharges, the variation of the intensities with gas pressure is calc., and curves are drawn for the relative intensities of the various lines at different pressures, and compared with experimental curves. From the general agreement an expression for the distribution is given. Results indicate that the energy distribution of the majority of the electrons is determined by diffusion, but a small fraction form a group with Maxwell energy distribution, and of predominating influence in the He discharge at high pressure as regards excitation and ionisation. N. M. B.

Energy losses of electrons striking the nitrogen nucleus. J. E. Roberts, R. Whiddington, and E. G. Woodroofe (Proc. Leeds Phil. Soc., 1936, **3**, 189—190).—When electrons of medium energy are passed through N_2 at low pressure, the scattered electrons, on analysis, show not only a strong line corresponding to elastic collisions without energy loss, but also bands corresponding to mol. excitations. Singlet transition bands are observed at higher impact energy (120 e.v.) and triplet bands at 16—25 e.v. The max. of these bands correspond approx. in some cases with known spectroscopic vals. J. W. S.

Concentration of electron beams by gases. I. Sokolskaja (Tech. Phys. U.S.S.R., 1936, **3**, 28—38).—The relations between the focal length and gas pressure, beam current, velocity, and wall potential in A were investigated. H. J. E.

Determination of electron velocity by means of probe measurements. W. Denecke and E. Lübcke (Physikal. Z., 1936, **37**, 347—350).—It is shown that by the use of several test wires arranged in a certain part of the positive column of a glow discharge it is possible to obtain the velocity distribution of electrons, the space potential, the electron c.d., and electron concn. A. J. M.

Change in secondary-electron emission of insulators and semi-conductors on irradiation with electrons. M. Knoll (Naturwiss., 1936, **24**, 345).—If an insulator is irradiated with electrons (500—5000 volts) there is a considerable change in the secondary-electron emission when tested with another electron beam. The secondary emission factor was lowered for Al_2O_3, glass, Cu_2O, and certain phosphors. A. J. M.

Scattering of positrons by electrons with exchange on Dirac's theory of the positron. H. J. Bhabha (Proc. Roy. Soc., 1936, *A*, **154**, 195—206).—Exchange may take place between the electron initially observed and one of the virtual electrons in states of negative energy. The process may be considered as one in which the initial electron and positron have been annihilated, giving rise simultaneously to a new pair. L. L. B.

Theory of the positron. A. Proca (Compt. rend., 1936, **202**, 1366—1368). R. S.

Production of electron pairs. J. C. Jaeger (Nature, 1936, **137**, 781—782).—The absorption cross-sections per atom for the production of positive–negative electron pairs by γ-rays have been determined for Sn, Tb, and Pb. The Born approximation gives vals. which are too low, but the error decreases rapidly with decreasing at. no. and increasing energy of the γ-rays. L. S. T.

Law of impulse maintenance with the annihilation of positrons. A. I. Alichanian, A. I. Alichanov, and L. A. Arzimovitsch (Compt. rend. Acad. Sci. U.R.S.S., 1936, **1**, 287—288, and Nature, 1936, **137**, 703—704).—A system of counter tubes was used to measure quanta set free on annihilation of positrons from radio-P (obtained by bombardment of Al with α-particles from Ra-C'). It was shown that two quanta are emitted in opposite directions as required by the impulse maintenance law. A. J. M.

At. wts. by calculation. A. C. Woodmansey (Phil. Mag., 1936, [vii], **21**, 1079—1081).—The at. wts. of simple elements are represented satisfactorily by the expression at. wt. $= 0{\cdot}9935x + 0{\cdot}0140y$, where x = mass no., y = at. no. J. W. S.

At. wt. of cadmium. O. Hönigschmid and R. Schlee (Z. anorg. Chem., 1936, **227**, 184—192).—The mean of eight argentometric titrations of $CdCl_2$ gives Cd 112·41±0·002 (Ag 107·880, Cl 35·457), and of five titrations of $CdBr_2$, 112·41±0·004. This val. is identical with the international at. wt., and differs from Aston's by 0·2 unit. F. L. U.

Revision of at. wt. of chromium. II. Study of the relations CrO_2Cl_2 : 2Ag and CrO_2Cl_2 : 2AgCl. F. González Núñez (Anal. Fís. Quím., 1935, **33**, 533—548; cf. A, 1930, 1337).—The at. wt. of Cr has been redetermined as 52·013±0·001. F. R. G.

Enrichment of nitrogen in the isotope ^{15}N. D. E. Wooldridge and F. A. Jenkins (Physical Rev., 1936, [ii], **49**, 704).—Further enrichment of ^{13}C by diffusion of CH_4 in a Hertz apparatus has been obtained (cf. this vol., 574). This method has been extended to N_2. Isotope band heads due to $^{14}N^{15}N$ had an intensity corresponding with an abundance of 3 at.-% ^{15}N, an enrichment factor of approx. 10. N. M. B.

Isotopic constitution of strontium, barium, and indium. J. P. Blewett and M. B. Sampson (Physical Rev., 1936, [ii], **49**, 778).—Mass spectrograph analyses of the ions of Sr, Ba, and In emitted when oxides of these elements are heated on W filaments give evidence of isotopes ^{84}Sr and ^{134}Ba, with abundance 0·5 and 1·8%, respectively. Other isotopes of Sr of masses 82, 83, 85, 89, and 90 were present to <1 in 2000, 1000, 2000, 500, and 2000, respectively, Ba isotopes of masses 132, 133, 139, and 140 to <1 in 2000, 1000, 400, and 1000, respectively, and In isotopes of masses 110, 111, 112, 114, 116, 117, 118, and 119 to <1 in 5000, 10,000, 5000, 200, 5000, 10,000, 8000, and 30,000, respectively (cf. Szilard, A., 1935, 276). N. M. B.

Proof of the existence of the odd cadmium isotopes by band spectroscopy. A. Heimer and E. Hulthen (Naturwiss., 1936, **24**, 377).—Examination of the CdH/CdD spectrum over the range 3300—3400 A. shows the presence (in order of intensity) of the following isotopes of Cd: 114, 112, 110, 111, 113, 116. A. J. M.

Isotope displacement in the arc spectrum of platinum. S. Tolansky and E. Lee (Nature, 1936, **137**, 908).—Even isotope displacements in the Pt I spectrum (tabulated) are in good agreement with the results of Jaeckel and Kopfermann (this vol., 654). ^{195}Pt has a nuclear spin of $\frac{1}{2}$, and approx. abundances of the isotopes 198, 196, 195, and 194 are 1 : 4 : 4 : 5. L. S. T.

Spontaneous and artificial transmutations of atom nuclei. K. C. Kar (Phil. Mag., 1936, [vii], **21**, 1067—1078; cf. A., 1934, 5).—Mathematical. The wave-statistical theory developed previously is extended to explain the emission of long range α-particles by radioactive elements and to explain artificial disintegration. J. W. S.

Collision forces between light nuclei. C. B. O. Mohr and G. E. Pringle (Nature, 1936, **137**, 865—866).—Calculations made from measurements of the angular distribution of scattering of the slower α-particles in H_2, D_2, and He indicate that the forces which come into play act at distances $>10^{-12}$ cm. If the current method of explanation is to be retained forces of range $>e^2/mc^2$ must be included. L. S. T.

Structure of neutrons and β-disintegration. D. Meksyn (Nature, 1936, **137**, 906).—It is assumed that when a neutron is formed from a proton and an electron the excess of energy of the particles is transformed into rest mass, energy and momentum being conserved. L. S. T.

Possible effect of screening in the theory of β-disintegration. M. E. Rose (Physical Rev., 1936, [ii], **49**, 727—729; cf. Konopinski, A., 1935, 1048).—Various considerations and calculations individually lead to the conclusion that the effect of screening is negligible. N. M. B.

End-points of the β-ray spectra of radium-*E* and thorium-*C″*. F. C. Champion and N. S. Alexander (Nature, 1936, **137**, 744).—The end-points occur at $1·35\times10^6$ and $2·25\times10^6$ e.v., respectively. L. S. T.

Excitation of γ-rays in boron. S. Kikuchi, H. Aoki, and K. Husimi (Nature, 1936, **137**, 745).—The emission of γ-rays from B in presence of slow neutrons is confirmed. L. S. T.

Scattering of neutrons by protons. M. Goldhaber (Nature, 1936, **137**, 824—825).—The mean free path of the neutrons obtained from D_2O bombarded by radio-Th is 4·5±1·5 cm. of paraffin. Disagreement with the theoretical val. of 1·3 shows that there is no evidence of the existence of an excited state of the deuteron and that another model of the proton–neutron interaction is required. L. S. T.

Experiments with neutrons produced by the bombardment of deuterons with deuterons. S. Kikuchi, S. Nakagawa, H. Aoki, and K. Fushimi (Proc. Phys.-Math. Soc. Japan, 1935, **17**, 189—193).—The Fermi photon effect has been studied with deuteron–deuteron neutrons. The production of slow neutrons and their absorption by various elements and salts have been studied. Fermi's results are confirmed. Ch. Abs. (*e*)

Properties of slow neutrons. B. Pontecorvo (Nuovo Cim., 1935, [ii], **12**, 211—222; Chem. Zentr., 1935, ii, 1312).—The activity effect of neutrons slowed down by passage through material containing H is much > that of neutrons slowed down by other materials (Pb, SiO_2, C). J. S. A.

Cross-section measurements with slow neutrons of different velocities. H. von Halban, jun., and P. Preiswerk (Nature, 1936, **137**, 905—906).—The cross-section for neutron capture by B decreases with increasing energy of the neutrons (cf. this vol., 402). Results for neutrons captured by Li, Dy, Ag, and Rh are also given. In general, cross-sections for resonance neutron capture and for capture of thermal neutrons are greatest for nuclei the resonance levels of which have the lowest energy. L. S. T.

Disintegration of boron by neutrons. R. J. Walen (Compt. rend., 1936, **202**, 1500—1502).—The results are in agreement with the equation $^{10}_{5}B+^{1}_{0}n\rightarrow^{7}_{3}Li+^{4}_{2}He+Q$. R. S.

Transformation of boron by slow neutrons. M. J. Deisenroth–Missovski, G. D. Latischev, L. I. Russinov, and R. A. Eichelberger (Compt. rend. Acad. Sci. U.R.S.S., 1936, **1**, 351—353).—The effect on the no. of transmuted particles in the nuclear reaction ${}^{10}_{5}B+{}^{1}_{0}n \rightarrow {}^{7}_{3}Li+{}^{4}_{2}He$, of layers of H_2O of various thicknesses interposed between the source of neutrons and the B compound (Me_3BO_3) was investigated. The curve between no. of transmuted particles and thickness of H_2O layer may be explained by supposing either that the neutrons are absorbed in the H_2O, or that the absorption of slow neutrons by B shows a resonance effect. A. J. M.

Absorption of slow neutrons in boron. F. Rasetti, D. P. Mitchell, G. A. Fink, and G. B. Pegram (Physical Rev., 1936, [ii], **49**, 777).—Using a method similar to that employed for Ag and Cd (cf. this vol., 264), the dependence of the capture cross-section on neutron velocity was determined. Results indicate that the absorption of thermal energy neutrons follows the $1/v$ law. N. M. B.

Disintegration of nitrogen by slow neutrons. T. W. Bonner and W. M. Brubaker (Physical Rev., 1936, [ii], **49**, 778).—The reaction is found to be ${}^{14}_{7}N+{}^{1}_{0}n \rightarrow {}^{14}_{6}C+{}^{1}_{1}H+Q_2$, giving the val. 0·58±0·03 m.e.v. for the energy of disintegration Q_2, calc. from range measurements, and eliminating a previous discrepancy (cf. this vol., 403; Chadwick, *ibid.*, 5). N. M. B.

Artificial radioactivity. K. Diebner and E. Grassmann (Physikal. Z., 1936, **37**, 359—383).—A review.

Induced radioactivity of short period. T. Bjerge (Nature, 1936, **137**, 865).—An arrangement for detecting induced radioactivity >0·3 sec. is described. When bombarded by a neutron source (Be+Rn) of 350 millicuries, Be gives a strong activity of 0·9±0·2 sec. half-val. period and max. energy of 6 to 8×10^6 e.v. The effect is not increased by surrounding the source with paraffin wax. The process leading to the active nucleus is discussed. No new activities were detected with Li, B, C, N, O, F, Na, Al, Cl, Fe, Ni, Cu, Zn, Se, Ag, Cd, Sn, or Pb. L. S. T.

Disintegration of boron into three α-particles. P. I. Dee and C. W. Gilbert (Proc. Roy. Soc., 1936, **A**, **154**, 279—296).—The disintegration of B by artificially accelerated protons takes place as follows: ${}^{11}_{5}B+{}^{1}_{1}H \rightarrow {}^{4}_{2}He+{}^{4}_{2}He+{}^{4}_{2}He$. The total energy released in the reaction is $8{\cdot}7\pm0{\cdot}2\times10^5$ e.v. A theoretical picture of the process, involving the existence of an unstable ${}^{8}_{4}Be$ nucleus, is given. L. L. B.

High-velocity positive ions. V. Disintegration of boron. VI. Disintegration of carbon, nitrogen, and oxygen by deuterons. J. D. Cockcroft and W. B. Lewis (Proc. Roy. Soc., 1936, **A**, **154**, 246—261, 261—279; cf. A., 1934, 826).—V. Experiments on the disintegration of B by deuterons of energy 300—600 kv. have established the existence of two homogeneous α-particle groups of range 4·5 and 14·7 cm. for deuteron energies of 560 kv. These groups are assumed to result from transmutations in which ${}^{8}Be$ and ${}^{9}Be$ are produced. Two continuous distributions of doubly charged ionising particles are also observed, probably due to the break up of the ${}^{10}B$–deuteron system into 3 α-particles.

VI. The disintegration of C, N, and O_2 by deuterons has been reinvestigated by an improved method. Several new groups of particles have been discovered, and all the reaction energies determined to within about 0·1 mv. The new results are used to correct Bethe's mass scale, and to check the energy balance in the process of positron emission from radio-N_2. L. L. B.

Separation of radioactive atoms from the stable isotopic atoms. O. Erbacher and K. Philipp (Z. physikal. Chem., 1936, **176**, 169—181).—The radioactive species of halogens produced by the action of neutrons on a liquid non-ionised org. halogen compound (I) are formed as ions and can be removed by shaking with H_2O. The (I) which dissolves in the H_2O at the same time is subsequently removed by extraction with C_6H_6, giving a practically pure aq. solution of the radioactive ions. In this way 10^{-16} g. of radioactive Br has been separated from 21 g. of inactive Br atoms. R. C.

Preparation of artificially radioactive halogens in unweighable amount from the stable isotopes. O. Erbacher and K. Philipp (Ber., 1936, **69**, [*B*], 893—898).—EtI, EtBr, or $C_2H_4Cl_2$ is bombarded (method to be described) and shaken with blood charcoal which is then introduced into H_2O through which H_2 bubbles in presence of Pt powder. When the mixture is boiled and filtered, the bulk of the radioactive halogen is contained in the H_2O, which remains clear after addition of $AgNO_3$ and dil. HNO_3. H. W.

Radioactive isotope of sulphur. E. B. Andersen (Z. physikal. Chem., 1936, **B**, **32**, 237—242).—A radioactive isotope of half-life period ~ 80 days and probably ${}^{35}_{16}S$ is formed by the action of neutrons on the Cl in CCl_4. It has been used to study the reactions of thiosulphates. R. C.

New transformation processes in the bombardment of uranium with neutrons. Elements beyond uranium. O. Hahn, L. Meitner, and F. Strassmann (Ber., 1936, **69**, [*B*], 905—919; cf. A., 1935, 1050).—The production of the following at. types is observed by the bombardment of U with neutrons; the half-life periods and type of bombardment are given in parentheses: ${}^{235}Th$ (4 min., slow); ${}^{235}Pa$ (very short, slow); ${}^{235}U$ (24±2 min., slow); ${}^{237}U$ (40 sec., rapid); ${}^{239}U$ (10 sec., preferably slow); ^{237}eka-Re (16±1 min., rapid); ^{239}eka-Re (2·2±0·2 min., preferably slow); ^{237}eka-Os (12 hr., rapid); ^{239}eka-Os (59±2 min., preferably slow); ^{239}eka-Ir (3 days, preferably slow); (?)eka-Pt (~3 hr., preferably slow). H. W.

Decrease of the primary cosmic radiation in different materials. J. Clay (Physica, 1936, **3**, 332—340).—Measurement of the decrease of ionisation by cosmic radiation under thick layers of Fe and Pb proves that equilibrium between primary radiation and secondary effects is reached under layers > 400 g. per sq. cm. Under such layers the decrease in Pb, Fe, and H_2O ∝ density, in accord with a corpuscular nature of the radiation. The coeff., however, is 0·00044 per g. per sq. cm., about one tenth of that in air. It is suggested that there are two independent types of primary radiation, both shower-producing, and to account for the decrease in intensity in H_2O layers at different magnetic latitudes it is assumed that the hard and soft components consist of protons and electrons, respectively, the energy required to penetrate the atm. being 4×10^9 e.v. for protons and about 10^{10} e.v. for electrons. J. W. S.

Range of a single shower particle produced by cosmic rays in lead, iron, and aluminium. J. Clay (Physica, 1936, 3, 352—358).—By arranging three counters under a shower-producing sheet, one being enclosed within an absorbing layer of variable thickness, and measuring the threefold coincidences of the counters, it has been shown that the particles have a definite range, which for Pb showers is 4·4 cm. in Pb, 5·6 cm. in Fe, and about 10 cm. in Al. Shower particles from Fe have a range of 5·2 cm. in Pb, whilst those from Al have still longer ranges. The calc. energies are 87, 104, and 168 ($\times10^6$) e.v. for Pb, Fe, and Al showers, respectively. J. W. S.

Absorption of cosmic-ray showers in lead. C. G. Montgomery and D. D. Montgomery. **Coincidence counter studies of cosmic-ray showers.** R. H. Woodward. **Geomagnetic analysis of cosmic radiation.** G. Lemaitre and M. S. Vallarta (Physical Rev., 1936, [ii], 49, 705—711, 711—718, 719—726; cf. A., 1935, 560). N. M. B.

Interpretation of Shankland's experiment. R. Peierls (Nature, 1936, 137, 904). L. S. T.

Wave theory of the neutrino. G. Rumer (Compt. rend., 1936, 202, 1484—1486; cf. A., 1935, 143). R. S.

Neutrino theory of light. M. Born and N. S. N. Nath (Proc. Indian Acad. Sci., 1936, 3, A, 318—337).—Mathematical. A general survey. N. M. B.

Constitution of atomic nuclei and their magnetic moments. S. Shimasaki (Proc. Phys.-Math. Soc. Japan, 1935, 17, 177—188).—It is assumed that protons or neutrons do not exist free in the nucleus, but only in the form of deuterons or ^3H nuclei. Two deuterons, two ^3H nuclei, or one deuteron and one ^3H nucleus have a tendency to unite. The nuclei of elements with $Z < 28$ are built principally by the addition of successive α-particles. In heavier elements additions of two ^3H nuclei play the chief rôle. Vals. for nuclear magnetic moments are calc. which are in agreement with experimental vals. Ch. Abs. (*e*)

Scattering and absorption of particles by nuclei. I. T. Sexl (Z. Physik, 1936, 99, 751—775).—Theoretical. A. B. D. C.

Statistical distribution of absorbed light quanta in the nuclei of a photographic layer. G. Ungar (Z. Physik, 1936, 99, 688—694).—Theoretical. A. B. D. C.

Fundamental equations of elementary particles. A. Proca (Compt. rend., 1936, 202, 1490—1492). R. S.

Interaction of two particles. H. R. Hulme (Proc. Roy. Soc., 1936, A, 154, 487—500).—The interaction of a nuclear particle in an excited state with an electron in the *K*-shell is considered according to the methods of quantum electrodynamics. L. L. B.

Inertia of electrons in metals. C. G. Darwin (Proc. Roy. Soc., 1936, A, 154, 61—66).—According to the theory of metals, the effective mass of the free electrons is increased owing to the displacement of their energy levels by the cryst. field. This effect is, however, not shown in experiments on electron inertia. L. L. B.

Wave functions for $1s2s\,^1S$ helium. A. S. Coolidge and H. M. James (Physical Rev., 1936, [ii], 49, 676—687).—Mathematical. N. M. B.

Ground state of lithium. H. M. James and A. S. Coolidge (Physical Rev., 1936, [ii], 49, 688—695).—Mathematical. Wave functions are examined. The calc. ionisation energy is $5·363\pm0·007$ against 5·364 e.v. observed. N. M. B.

Rational nomenclature for elementary corpuscles. P. Gruner (Physikal. Z., 1936, 37, 350—351).—The following names are proposed for corpuscles of mass approx. 10^{-27} g. (present names in parentheses): nulliton (neutrino), positon (positron), negaton (electron); and for particles of mass about 10^{-24} g. (general name, materion), proton (proton), neproton (negatively charged particle with the mass of the proton), neutron (neutron). A. J. M.

Validity of the Franck–Condon principle for evaluation of intensity distribution in molecular spectra. W. Finkelnburg (Z. Physik, 1936, 99, 798—800).—This principle cannot be applied to transitions involving loosely linked bonds or states of repulsion. A. B. D. C.

Intensity and form of the absorption bands of liquid oxygen. R. Guillien (Compt. rend., 1936, 202, 1373—1375; cf. A., 1934, 581).—The liquid O_2 bands 7635, 6290, 5769, 5325, 4773, and 4472 A. have been studied and compared with data for compressed O_2. R. S.

The *A* band of liquid oxygen. R. Guillien (Compt. rend., 1936, 202, 1423—1425).—The band extends from <7595 to 7735 A. Extinction coeffs. (κ) have been measured in liquid N_2–O_2 mixtures. The $\kappa/\kappa_{max.}$–$1/\lambda$ curve becomes narrower with increasing dilution. Data are recorded and discussed. L. J. J.

Influence of temperature on the absorption spectrum of ozone. E. Vassy (Compt. rend., 1936, 202, 1426—1428).—The spectrum is independent of pressure. The ratio of the extinction coeffs. at 20° and −80° for λλ 3372—3151 A. are recorded. There is no temp. effect at the absorption max. 85% of the atm. O_3 is at <11 km. altitude. L. J. J.

Band spectrum of the sulphur molecule. E. Olsson (Nature, 1936, 137, 745).—The internuclear distance of the S mol. obtained from the rotational analysis of six main absorption bands is 1·88 A.; this should replace the accepted val. of 1·60 A. L. S. T.

Absorption spectrum of water, aqueous solutions, and alcohols between 0·70 and 0·95 μ. E. Ganz (Ann. Physik, 1936, [v], **26**, 331—348).—The effect of temp. on the absorption bands of H_2O at 0·77 and 0·845 μ has been investigated. The displacement of the absorption max. at 0·77 μ with temp. shows a discontinuity at 40—45°, in common with many other properties of H_2O. The absorption const. at the max. ∝ thickness of H_2O. The absorption is considerably affected by ions (cf. following abstract). The quasicryst. structure of H_2O is established by small ions, but distorted by large ones. The absorption spectra of MeOH, EtOH, $Pr^{\alpha}OH$, and $Bu^{\alpha}OH$ have also been investigated. A. J. M.

Effect of temperature on the absorption bands of water in salt solutions. E. Ganz and W. Gerlach (Physikal. Z., 1936, **37**, 358—359).—The displacement and sharpening of the H_2O absorption band at 0·762 μ by raising the temp. from 10° to 90° have been investigated both for pure H_2O and for aq. solutions. The band is strengthened but not displaced in chloride solutions, whilst it is sharpened and displaced towards shorter λλ in nitrate, chlorate, and particularly perchlorate solutions. The effect of temp. on the position of the absorption max. is directly connected with the displacement of the max. caused by addition of salt at lower temp. There is equivalence between the effect of temp. and of ions on the structure of H_2O. A. J. M.

Collision potentials of C^+ and C^{++} ions in CO_2 deduced from $D(CO)=6·9$ volts. R. Schmid (Z. Physik, 1936, **99**, 626—632).—A dissociation energy of 6·9 volts for CO gives the potential of C^+ and C^{++} over the CO_2 ground level as 29 and 54 volts, respectively. CO_2 dissociates thus: $CO_2+5·47$ volts $\rightarrow CO(X^1\Sigma)+O(^3P)$, $CO(X^1\Sigma)+6$ volts $\rightarrow CO(a^3\Pi)$, and $CO(a^3\Pi)+5·22$ volts $\rightarrow C(^5S)+O(^3P)$. A. B. D. C.

Stark effect on absorption bands of nitric oxide. G. Blet (Rev. Opt. théor. inst., 1935, **14**, 62—67; Chem. Zentr., 1935, ii, 1315).—No broadening of the rotational lines in the band of NO at 2260 A. was observed. J. S. A.

Band spectra of the hydrides of lithium. III. Potential curves and isotope relations. F. H. Crawford and T. Jorgensen, jun. (Physical Rev., 1936, [ii], **49**, 745—752; cf. A., 1935, 1051).—Theoretical. N. M. B.

Band spectra of alkaline-earth hydrides. B. Grundström (Z. Physik, 1936, **99**, 595—606).—Rotation analysis and heats of dissociation are given for CaH, SrH, BaH, and MgH; the latter are 15,000, 14,000, 13,000, and 23,000 cm.$^{-1}$, respectively. A. B. D. C.

Absorption spectrum of aqueous chlorine and hydrogen peroxide vapour. W. C. Fergusson, L. Slotin, and D. W. G. Style (Trans. Faraday Soc., 1936, **32**, 956—962).—Data are recorded for the extinction coeffs. of aq. Cl_2 and HOCl solutions, and of HOCl and H_2O_2 vapours, for a no. of λλ > 210 mμ. L. J. J.

Continuous absorption spectrum of hydrogen iodide. C. F. Goodeve and A. W. C. Taylor (Proc. Roy. Soc., 1936, **A**, **154**, 181—187).—The extinction coeffs. of HI have been measured, and the approx. course of the upper potential energy curve is calc. from the eigenfunction of the ground state and the observed extinction. The results favour the dissociation into normal atoms. L. L. B.

Band spectrum of boron fluoride. H. M. Strong and H. P. Knauss (Physical Rev., 1936, [ii], **49**, 740—744; cf. Dull, A., 1935, 562).—The spectrum of BF excited by the electrodeless discharge in BF_3 has been photographed at high and low dispersion. 16 bands, degraded to the violet, were observed in the range λλ 3712—2580, resembling the CO bands corresponding with similar electronic configurations. Data and a vibrational analysis are given. N. M. B.

Band systems and structure of SiF. R. K. Asundi and R. Samuel (Proc. Indian Acad. Sci., 1936, **3**, A, 346—359).—A detailed analysis, using the experimental data of Johnson (cf. A., 1927, 1005), is given. N. M. B.

Absorption spectra of halides and oxyhalides of sulphur, selenium, and tellurium. S. L. Hussain and R. Samuel (Current Sci., 1936, **4**, 734—736).—Data are recorded for absorption max. and long-λ limits, agreeing with linking energies calc. from thermochemical data. Different absorption regions in the di- and tetra-halides correspond with splitting off of one and two halogen atoms, whilst in the oxychlorides two halogen atoms are split off simultaneously. The linking energies are approx. additive. L. J. J.

Absorption spectra of sodium and potassium in melts of their halogen salts. E. Mollwo (Nachr. Ges. Wiss. Göttingen, 1935, [ii], **1**, 203—207; Chem. Zentr., 1935, ii, 1510—1511).—The melts show broad absorption bands the position of which depends on the metal alone, being at 790 mμ for Na halides and 980 mμ for K halides. No simple relation exists between these bands and the absorption spectrum of the colour centres in the solid crystals. J. S. A.

Absorption spectra and linkage of inorganic salts in the vapour state. M. I. Haq and R. Samuel (Nature, 1936, **137**, 907—908; cf. this vol., 661).—The absorption spectra of H_2SO_4, K_2SO_4, Ag_2SO_4, and $ZnSO_4$ in the vapour state indicate covalent linking in this state. The suggested structural formula for NH_4NO_3 is $(O\!\!:)_2N·O·N(H)_4$ with 5 covalent linkings in the vapour state. L. S. T.

Spectral study of phenylhydrazine and derivatives. (Mlle.) D. Biquard (Bull. Soc. chim., 1936, [v], **3**, 909—916).—Ultra-violet absorption spectra of derivatives of $NHPh·NH_2$ and some aromatic diamines have been determined. Complex chromophores are indicated. E. S. H.

Effect of *X*-rays on methylene-blue and on trimethylthionine. W. Stenström and H. R. Street (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1498—1500).—Absorption by both dyes is reduced, reduction in methylene-blue being > in trimethylthionine. R. N. C.

Ultra-violet absorption spectra of certain proteins and amino-acids. C. B. Coulter, F. M.

Stone, and E. A. Kabat (J. Gen. Physiol., 1936, **19**, 739—752).—The absorption spectra (2500—3000 A.) of a no. of proteins consist of 6—9 bands similar to those of tryptophan, tryosine, and phenylalanine shifted 10 to 35 A. towards longer λ. That of pneumococcus type I antibody is similar to that of ψ-globulin. H. G. R.

Effect of solvents on the spectral curve of vitamin-A.—See this vol., 763.

Absorption spectra of œstrone and related compounds in alkaline solution. R. K. Callow (Biochem. J., 1936, **30**, 906—908).—Addition of NaOH to solutions of œstrone (I), œstradiol, and œstriol causes a shift of the ultra-violet absorption band towards the visible region but on the Me ether of (I) has no effect. The change is due to salt formation of the phenolic group in the 3 position and with (I) is not due to enolisation of the 17-keto-group. P. W. C.

Absorption spectra of dipheneins.—See this vol., 723.

Christiansen filter effect in the infra-red. R. B. Barnes and L. G. Bonner (Physical Rev., 1936, [ii], **49**, 732—740).—Prep., characteristics, and factors affecting data from the use of the filters are discussed. Results and curves are given for MgO, quartz, calcite, marble, $CaSO_4$, the halides of Na, K, and Rb, LiF, CsCl, CsBr, TlCl, TlBr, and TlI dispersed in air, and for quartz, MgO, and NaCl dispersed in org. liquids. Transmission between 3 μ and 90 μ was measured. N. M. B.

Infra-red spectra of H_2S, HDS, and D_2S. C. R. Bailey, J. W. Thompson, and J. B. Hale (Physical Rev., 1936, [ii], **49**, 777).—Data are contrasted and compared with those found by Nielsen (cf. this vol., 545). N. M. B.

Spectra [of substituted methanes] in the near infra-red. C. Corin (J. Chim. phys., 1936, **33**, 427—428).—Data are recorded for CH_4, MeCl, CH_2Cl_2, $CHCl_3$, and C_6H_{14} from 0·88 to 2·7 μ. The bands can be derived as harmonics or combinations of the four fundamental frequencies of the Raman spectra. R. C. M.

Extreme infra-red dispersion of polar and non-polar liquids. C. H. Cartwright and J. Errera (Proc. Roy. Soc., 1936, A, **154**, 138—157).—The absorption and reflexion of several polar and non-polar liquids have been measured between λλ of 50 and 150 μ. Vals. calc. for the at. polarisation were in good agreement with those determined for mols. in the gaseous state. The relaxation times and apparent radii of the polar mols. were calc. from measurements on the abs. intensity of absorption. On diluting the liquids in non-polar solvents, a characteristic absorption band in H_2O disappeared; this is therefore attributed to a quasi-cryst. structure. In all the other substances, however, the characteristic absorption bands remained in dil. solution, and are therefore due to intramol. vibrations. L. L. B.

Raman spectra of "heavy" arsine, silicochloroform, and silicobromoform. J. M. Delfosse (Nature, 1936, **137**, 868).—Frequencies are recorded. L. S. T.

Raman spectra of carbon and silicon tetrafluorides. D. M. Yost, E. N. Lassettre, and S. T. Gross (J. Chem. Physics, 1936, **4**, 325).—Data are recorded for liquid and gaseous states. L. J. J.

Influence of temperature on Raman bands of water at $\Delta\nu=510—780$ cm.$^{-1}$ G. Bolla (Nuovo Cim., 1935, [ii], **12**, 243—246; Chem. Zentr., 1935, ii, 1316).—The bands do not disappear with rise of temp. (cf. Magat, A., 1934, 1056). J. S. A.

Raman spectrum and electrolytic dissociation of selenic acid. C. S. Venkateswaran (Proc. Indian Acad. Sci., 1936, **3**, A, 307—317; cf. this vol., 547; Ganesan, A., 1935, 11).—Raman data are given for the state of solid, liquid, and aq. solution of concn. range 92·5—7·5 wt.-%. Marked changes in the position, intensity, and character of the lines are attributed to dissociation steps $H_2SeO_4 \rightarrow HSeO_4'+H^{\cdot}$ and $HSeO_4' \rightarrow SeO_4''+H^{\cdot}$, the first stage starting from the solid and the second stage from about 50% concn. Results are compared with those for H_2SO_4 (cf. Bell, A., 1935, 807) and conclusions on structure and apparent band shifts are drawn. Changes in the lines during solid–liquid transition are characteristic of heteropolar linkings in the acid mols. N. M. B.

Raman effect in liquid ammonia and solutions of nitrates in liquid ammonia. G. Costeanu (Compt. rend., 1936, **202**, 1432—1434).—A new line, 3460 cm.$^{-1}$, in liquid NH_3 is recorded. Dissolution of NH_3 in H_2O produces a shift of +10—15 cm.$^{-1}$ for the lines 3210, 3300, 3380 cm.$^{-1}$ The line 1048 cm.$^{-1}$ of NO_3' in H_2O solution is displaced towards shorter λ in NH_3 solution. L. J. J.

Raman effect and its applications in organic chemistry. II. A. Dadieu (Angew. Chem., 1936, **49**, 344—349).—A review. H. J. E.

Raman spectrum of deuterobromoform. O. Redlich and W. Stricks (Monatsh., 1936, **67**, 328—331; cf. A., 1935, 685).—The Raman spectrum of $CDBr_3$ has been measured and compared with that of $CHBr_3$, the relationship being in accord with the authors' theory. Comparison of data for PH_3 and PD_3 indicates that there are missing frequencies for PH_3 between 550 and 780 cm.$^{-1}$ and for PD_3 between 790 and 1115 cm.$^{-1}$ J. W. S.

Raman effect and dipole moment in relation to free rotation. III. Raman spectra of solid ethylene halides. S. Mizushima, Y. Morino, and S. Noziri (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, **29**, 63—70; cf. A., 1935, 428).—The Raman spectra and dipole moments of solid and liquid $C_2H_4Cl_2$ and $C_2H_4Br_2$ have been determined. It is concluded that the *trans*-configuration is adopted in the solid state, whilst in solutions the deviation from the *trans*-position varies with the solvent. R. S.

Raman spectra of metallic formates and constitution of formic acid. C. S. Venkateswaran (Current Sci., 1936, **4**, 736—737; cf. this vol., 268).—A reply to Halasyam (*ibid.*, 663). Raman spectral evidence for the presence of the ·CHO group in HCO_2H is summarised. L. J. J.

Deuterium compounds. II. Raman spectra of deuteroacetic acid and deuteroacetone. W.

Engler (Z. physikal. Chem., 1936, **B**, 32, 471—474).—The spectra of AcOD, $CD_3 \cdot CO_2D$, and $CO(CD_3)_2$ have been determined. R. C.

Raman spectrum of oxalic acid. J. H. Hibben (J. Chem. Physics, 1936, **4**, 323—324).—Polemical against Angus and Leckie (this vol., 269). L. J. J.

[Raman spectrum of oxalic acid.] W. R. Angus and A. H. Leckie (J. Chem. Physics, 1936, **4**, 324).—A reply to the above. L. J. J.

Raman spectra of β-methyl-Δ^{α}- and -Δ^{β}-butene.—See this vol., 819.

Raman effect. LV. *cyclo*Pentyl derivatives. K. W. F. Kohlrausch, A. W. Reitz, and W. Stockmair (Z. physikal. Chem., 1936, **B**, 32, 229—236).—The Raman spectra of *cyclo*pentanone and C_5H_9X (X=OH, NH_2, Me, SH, Cl, Br, I) have been determined. The effect of substitution differs characteristically from that in *cyclo*hexyl derivatives (this vol., 547), which is ascribed to the two C·H linkings of each CH_2 group being equiv. in direction in a flat C_5 ring, but not in a non-planar C_6 ring. The no. of lines suggests that the *cyclo*hexyl halogen derivatives exist in two forms different in configuration. R. C.

Raman spectra of compounds belonging to the anethole, safrole, and eugenol groups. B. Susz, E. Perrottet, and E. Briner (Helv. Chim. Acta, 1936, **19**, 548—558).—Raman spectra are given for estragol, natural anethole (I) (=isomerised estragol), safrole, *iso*safrole, heliotropin, eugenol and its Me and Et ethers, *iso*eugenol (II) and its Me ether, vanillin and its Me ether (cf. A., 1935, 1446). They show the frequencies characteristic of the Ph nucleus, aliphatic and aromatic C·H, C:O, and C:C (in $CH_2R \cdot CH:CH_2$ 1638, in CHR:CHMe 1654 cm.$^{-1}$) linkings. (I) probably contains 100% *trans*-, (II) 80% *trans*- and 20% *cis*-compounds. R. S. C.

Raman effect. LVI. Raman effect and free rotation. IV. K. W. F. Kohlrausch and (Gross Prinz) Ypsilanti (Z. physikal. Chem., 1936, **B**, 32, 407—416).—The Raman spectra of various straight-chain compounds, principally of the type $X \cdot [CH_2]_3 \cdot Y$, have been determined. The results show that if the mol. of a dihalogenated paraffin with a four- or five-membered chain is of such character that by free rotation various spatial forms may be realised the no. of lines in the vibrational spectrum is increased. $(CHBrMe \cdot)_2$ apparently exists only in a *trans* form; the Me groups appear to give this form the preponderating stability. R. C.

***cyclo*Propane. Raman spectrum and polymerisation by ultra-violet light.** L. Harris, A. A. Ashdown, and R. T. Armstrong (J. Amer. Chem. Soc., 1936, **58**, 852—853).—The Raman spectrum of *cyclo*propane (I) consists of 14 frequencies (cf. Lespieau *et al.*, A., 1932, 675; Kohlrausch and Köppl, A., 1934, 942); the strongest is at 1191 cm.$^{-1}$ A Hg-sensitised polymerisation of (I) to a viscous oil, b.p. about 300°/760 mm., occurs with Hg-radiation of λ 2536 A. H. B.

Raman spectrum of some substituted *cyclo*hexenes. E. Canals, M. Mousseron, L. Souche, and P. Peyrot (Compt. rend., 1936, **202**, 1519—1521).—The Raman spectra of 1-methyl-, -ethyl-, -propyl-, -*iso*propyl-, -butyl-, -phenyl-, -benzyl-, and -*cyclo*hexyl-Δ^1-*cyclo*hexene (I) are similar to those of other *cyclo*hexenes (cf. A., 1934, 10). The line 825 cm.$^{-1}$ of *cyclo*hexene is replaced by two in the regions 747—772 and 825—850, and in the Me, Et, and Pr derivatives the frequency of the line 758 varies inversely as the no. of C. The line 1440, characteristic of CH_2, is accompanied by a satellite 1453 in all cases except (I) which gives one line at 1443. R. S.

Raman effect and problems of constitution. X. Strain theory. K. W. F. Kohlrausch and R. Seka (Ber., 1936, **69**, [*B*], 729—743).—Measurements are recorded for *cyclo*hexene, *cyclo*pentane (I), *cyclo*pentene, *cyclo*pentadiene, α-di*cyclo*pentadiene (II) and its H_2- and H_4-derivatives, Me_2 α-*cis*-3 : 6-*endo*methylene-Δ^4-tetra- and -hexa-hydrophthalate, Me 2 : 5-*endo*methylene-Δ^3-tetra- and -hexa-hydrobenzoate. The transition of (I) to *cyclo*propane, which according to model is accompanied by an increase in strain and according to thermochemistry by an increase in energy, involves a decrease in strength of the C·C linking when the spectra are evaluated by an approx. theoretical treatment of the vibration forms; the corresponding increment of the energy content is of the same order of magnitude as that determined thermochemically. In the unsaturated plane, five-membered ring for which the approx. strain in the ring according to model and, in particular, the deformation of the angle at the double linking cannot account for the increased energy content, the C:C frequency suffers a depression, probably mainly due to a diminution in the strength of the double linking. Different frequencies are shown by the two double linkings in (II) one of which is situated (Alder–Stein) in the slightly strained *cyclo*pentene ring, whereas the other belongs to the greatly strained di*cyclo*heptene ring. In this case the deformation of the angle at the double linking in the strained ring is not calculable, but the increase of its energy content is thermochemically established. The lower C:C frequency is due to the more slightly strained ring. The calc. increase of the energy content from the depression of the frequency agrees in order of magnitude with the results obtained thermochemically. H. W.

Nature of intermolecular oscillations in some organic crystals. S. C. Sirkar (Indian J. Physics, 1936, **10**, 109—116).—The Raman spectra of $C_{10}H_8$ and Ph_2O have been investigated in the solids and in solution in MeOH and C_6H_{12}, at different temp. Certain of the Raman lines of these substances seem to be due to intermol. vibrations in groups of mols. which persist in the case of Ph_2O, but disappear almost completely in the case of $C_{10}H_8$ when the substance is melted or dissolved. The directions of the displacements of the $C_{10}H_8$ lines with temp. are in agreement with the lattice oscillation theory of Gross and Vuks (A., 1935, 564, 914), but the extent of the displacement is different for different lines, and is too great to be explained by this theory. The absorption spectra of Ph_2O and $C_{10}H_8$ in the solids and in solution in MeOH and C_6H_{12} have also been investigated.

The positions of the bands for solid $C_{10}H_8$ are different from those for solutions or vapour, but in the case of Ph_2O there is no appreciable difference in the absorption spectra of the solid, liquid, or solution. This may be due to the polar character of Ph_2O, which would allow the formation of stable polymerised groups, not completely broken down even in solution. A. J. M.

Raman spectra and decomposition reactions of ozonides.—See this vol., 839.

Variation of intensity of scattered light with temperature. C. V. Jogarao (Proc. Indian Acad. Sci., 1936, **3**, **A**, 377—383).—The intensity of scattering increases in C_6H_6 and AcOH, and decreases in $PhNO_2$ and HCO_2H, with rise of temp. The differences are due to the aggregate effect of density scattering and orientation scattering; on separation, the former always increases with temp., and the latter sometimes increases (C_6H_6) and sometimes decreases ($PhNO_2$, AcOH, and HCO_2H). N. M. B.

Mechanism of the emission of light by chemical reactions. R. Audubert (Compt. rend., 1936, **202**, 406—407; cf. this vol., 407).—It is suggested that mols., after reaction, may retain both their energy of activation and the energy of reaction, and that their subsequent collisions of the fourth kind may give rise to the emission of quanta of high energy. Calculations for certain reactions are in accord with experiment. J. W. S.

Emission of ultra-violet light during the anodic oxidation of aluminium. R. Audubert and O. Viktorin (Compt. rend., 1936, **202**, 1504—1507; cf. A., 1935, 1055).—The intensity of the ultra-violet light emitted decreases with time. There is no emission from an Al cathode. R. S.

Thermoluminescence and chemiluminescence. H. Steinmetz and M. Alt (Z. Krist., 1936, **92**, 363—371).—These effects are discussed for several cases, especially the influence of impurities and the separation of chemical from thermal effects. B. W. R.

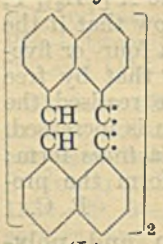
Fluorescence of terbium salts in solutions. A. Filippov, J. Larionov, and A. Seidel (Compt. rend. Acad. Sci. U.R.S.S., 1936, **1**, 253—256).—The fluorescence spectrum of aq. solutions of salts of the Y series of earths is ascribed entirely to Tb^{+++}. The intensity of the fluorescence depends largely on the method of prep. of the solution, being increased by heating the salt before dissolution, and destroyed by the presence of traces of HNO_3. The method may be used in the detection of traces of Tb. A. J. M.

Inhibition of the fluorescence of methylene-blue by ferrous salts. K. Weber (Naturwiss., 1936, **24**, 318).—The observation of Hellström (this vol., 270) that the fluorescence of methylene-blue is inhibited by $Fe^{\cdot\cdot}$ ions is related to the fading of vat dyes when illuminated in presence of $Fe^{\cdot\cdot}$ ions (cf. this vol., 300), both being dependent on the more positive redox potential of the activated dye mol. (or ion) and its consequent reaction with $Fe^{\cdot\cdot}$. The variation of the effect with p_H is attributed to the influence of the latter on the redox potential of the dye and of the ferro–ferrous system. W. O. K.

Phosphorescence and long-period fluorescence of organic dyes. P. Pringsheim and H. Vogels (J. Chim. phys., 1936, **33**, 345—355).—Measurements of the decrease of intensity of light emitted by trypaflavine adsorbed on SiO_2 gel, when activation ceases, in high vac. at 39°, 18·5°, −37°, and −190° show that at −190° the emission is a long-period fluorescence, whilst at the higher temp. it is a true phosphorescence in agreement with Jablonski (A., 1935, 682). R. C. M.

Fluorescence of porphyrins. II. A. Stern and H. Molvig (Z. physikal. Chem., 1936, **176**, 209—225; cf. this vol., 270).—Fluorescence spectra in dioxan have been determined. The displacement of the fluorescence band max. caused by partial alkyl substitution of the porphin system (I) is not always in the same direction as the displacement of the absorption max. The effect on the fluorescence of hydrogenation of the vinyl groups of (I) and the dihydroporphin system has been examined. Me chlorophyllide *a* has a fluorescence spectrum of four bands, showing that Mg has a considerable effect on the fluorescence. The considerable similarity in the fluorescence spectra of βδ-di-iminocoproporphyrin II Me_4 ester (II) (this vol., 86) and coproporphyrin II Me_4 ester shows that (II) must have a porphyrin structure and therefore contain *tert.* N. In aq. HCl solution (II) does not fluoresce, presumably due to salt formation at the βδ-N atoms. Pyrromethenes do not fluoresce in HCl. It appears that fluorescence in the visible is caused by the presence of the pyrromethene structure in (I). When fluorescence is absent in HCl solution it may be inferred that N is present instead of the methene groups of (I). In porphyrins substituted only with alkyl there is present the same (I) as in all other normal porphyrins, and not a special form of (I). The fluorescence of the porphyrins is caused by the conjugated pyrrolenine nuclei, and the fluorescence spectrum is affected by the smallest changes in this structure. R. C.

Fluorescence and duration of emission of fluorocyclene. M. Makoviecka (Acta. phys. polon., 1934, **2**, 357—359; Chem. Zentr., 1935, ii, 1336).—The fluorescence of fluorocyclene (I) in various solvents varies little with the solvent, and the spectral distribution of intensity is independent of the exciting λ. All four fluorescence bands exhibit the same degree of polarisation; at low temp. they become narrower and displaced towards longer λ. The mean duration of emission is 2·9 × 10^{-7} sec. J. S. A.



(I.)

Methods of determining the Volta effect. H. Gericke (Physikal. Z., 1936, **37**, 327—338).—A crit. examination of the ionisation, condenser, photoelectric, and thermionic methods is given. A. J. M.

Determination of the Volta effect for pure metals. F. Krüger and G. Schulz (Ann. Physik, 1936, [v], **26**, 308—330).—The Volta effect was measured for a series of metals by a photo-electric method. For W, Ta, Fe, Ni, Ag, Cu, and Mo the effect disappeared when the metals were completely outgassed by long heating in vac., and reappeared when the treated metals were allowed to remain in damp air. This supports the chemical theory of the effect. The photo-electric effect was also determined for these metals. The effect of heating in vac. was similar to that on the Volta effect, except at the beginning of the heating, where the photo-effect increases on removal of H_2O and gases from the metal whilst the Volta effect at once diminishes, being dependent only on the H_2O film. A. J. M.

Photo-electric investigations of semi-conductors. G. Bergmann and J. Hänsler (Z. Physik, 1936, **100**, 50—79).—Electrons in many semi-conductors move under the influence of light alone. Spectral sensitivities of these substances show max. that move to increased λ with increased mol. wt., provided the ions in question come from one column of the periodic table. A. B. D. C.

Photo-effect for thin layers of aluminium and tantalum oxide. G. Rosenthal (Z. Physik, 1936, **99**, 607—621).—Ta oxide cells give greater photo-effects than the Al cells. A. B. D. C.

Photo-electric sensitivity of palladium–silver alloys saturated with hydrogen. F. Krüger and W. Kallenbach (Z. Physik, 1936, **99**, 743—750).—Max. sensitivity occurs at 20% Ag with a subsidiary max. at 60 to 65% Ag, and these coincide with alloys of max. H_2 absorption (cf. Schniedermann, A., 1932, 789). A. B. D. C.

Internal photo-effect in potassium chloride under illumination with ultra-violet light. N. Kalabuchov (Compt. rend. Acad. Sci. U.R.S.S., 1936, **1**, 251—252).—On the basis of an energy scheme due to Tartakovski (A., 1935, 1306) it is to be expected that the internal photo-effect will occur with the allochromatic crystals NaCl and KCl without preliminary treatment, when they are irradiated by λ 1602 and 1841 A., respectively. This effect has been observed with KCl crystals using a H_2 discharge tube with CaF_2 window as light source. A. J. M.

Crystal photo-effect for coloured Rochelle salt. F. Seidl (Z. Physik, 1936, **99**, 633—634).—Rochelle salt coloured by radioactive radiation shows a secondary photo-effect. A. B. D. C.

Nature of the surface conduction of cuprous oxide. L. Dubar (Compt. rend., 1936, **202**, 1330—1332; cf. A., 1935, 1055).—The surface conduction is negligible after removing gas or forming a fresh surface in vac. H. J. E.

Normal conductivity and reversion effects of solid paraffin subject to γ-rays. F. Seidl (Z. Physik, 1936, **99**, 695—709).—γ-Radiation increases normal conductivity and influences reversion phenomena. The greatest resistance of paraffin of m.p. 52—53° is $3{\cdot}3\times10^{18}$ ohm cm. A. B. D. C.

Electrical conductivity of oxides of cobalt and iron. Recrystallisation of zinc oxide. C. Wagner and E. Koch (Z. physikal. Chem., 1936, B, **32**, 439—446).—The sp. conductivity, κ, of CoO and FeO at 800—1000° increases with the O_2 pressure, *p*; conduction is of the electron deficiency type (cf. A., 1933, 888). For Co_3O_4, Fe_3O_4, and Fe_2O_3 at 900—1000° κ is practically independent of *p*. For Co_3O_4 at room temp. κ varies with the previous treatment, *i.e.*, depends on the presence of an excess of O, which varies with the temp. at which equilibration with the gas phase was last effected previously. The conductivity at high temp. is ascribed to the distribution of $Co^{\cdot\cdot}$ and $Co^{\cdot\cdot\cdot}$ ions being partly irregular. When heated in H_2 at 450° ZnO undergoes recrystallisation to a greater extent than if heated in O_2 owing to both its elements being transportable through the gas phase as at. Zn and H_2O. R. C.

Liquid ammonia as a solvent. VI. Dielectric constant of liquid ammonia. H. M. Grubb, J. F. Chittum, and H. Hunt (J. Amer. Chem. Soc., 1936, **58**, 776).—Vals. at 5°, 15°, 25°, and 35° are 18·94, 17·82, 16·90, and 16·26, respectively. E. S. H.

Determination of the dielectric constants of organic liquids at radio frequencies. II. Chlorobenzene and ethylene dichloride. R. M. Davies (Phil. Mag., 1936, [vii], **21**, 1008—1029; cf. this vol., 271).—The dielectric consts. of PhCl and $C_2H_4Cl_2$ at 20°, 25° were $5{\cdot}713_5$, $5{\cdot}626_3$ and $10{\cdot}64_7$, $10{\cdot}35_8$, respectively. H. J. E.

Dispersion and absorption by viscous liquids at high frequencies. W. Dahms (Ann. Physik, 1936, [v], **26**, 177—192).—Dielectric consts. and conductivities of fructose (I) and sucrose (II) solutions and $PhNO_2$ for λλ 1·47—8·30 m. have been measured by Wenk's method (A., 1933, 925). The results with $PhNO_2$ agree with Debye's theory. With the sugars, the dipole conductivity increases more slowly than $\propto 1/\lambda^2$, whilst at short λ, ε is < the statistical val. in the case of (I), but not of (II). L. J. J.

Apparent dipole moments of benzene, *p*-dichlorobenzene, diphenyl, 4 : 4′-dichlorodiphenyl, and carbon disulphide in polar solvents. C. G. Le Fèvre and R. J. W. Le Fèvre (J.C.S., 1936, 487—491; cf. this vol., 140).—The dielectric consts. and *d* of solutions of the above substances in C_6H_6, $CHCl_3$, CCl_4, PhCl, $PhNO_2$, $NPhMe_2$, EtOBz, and PhCN have been determined. Assuming that the usual evaluation of dipole moments is valid for these cases, the data indicate that the induced moments of the solute ∝ the dipole moment of the solvent, approx. The results suggest that the dipolar solvent units cluster around the solute with their dipoles in parallel rather than antiparallel alinement. The model leads to polarisabilities of the solute mols. in general accord with other vals. Alternative interpretations are discussed. J. G. A. G.

Solvent effect in dipole-moment measurements. Polarisations of chloro- and nitrobenzene, chloroform, and bromoform in polar solvents. R. J. W. Le Fèvre and P. Russell (J.C.S., 1936, 491—495; cf. this vol., 140).—Dielectric consts. and *d* of binary mixtures of the above substances and of binary mixtures with C_6H_6 and PhMe have been determined, and polarisations, *P*, and apparent dipole moments, μ, calc. The tendency towards organised structure in liquids leads to models whereby the effects on *P* and μ of the mutual interaction of the mols. may be inferred. In conformity with the theory, the μ of $PhNO_2$ and PhCl, separate and mixed, in the liquid state are $<$ in the gas state. The μ of $PhNO_2$ and PhCl are slightly depressed by dissolution in $CHCl_3$, but the μ of $CHCl_3$ and $CHBr_3$ are raised by dissolution in $PhNO_2$ and PhCl. J. G. A. G.

Apparent dipole moment of paraldehyde in various solvents. R. J. W LE FÈVRE and P. RUSSELL (J.C.S., 1936, 496—497).—The dielectric consts. and *d* of paraldehyde (I) and solutions of (I) in nine polar and non-polar solvents have been determined. Polarisations have been calc. The apparent dipole moment in the solvents is 1·68—2·26 *D*, that of (I) alone being 1·89 *D*. J. G. A. G.

Refraction and dispersion of gases and vapours. VIII. Variation with temperature of molecular refraction of carbon dioxide and acetic acid vapour. H. GOLDSCHMIDT and P. HÖLEMANN (Z. physikal. Chem., 1936, **B**, **32**, 341—352; cf. A., 1934, 348).—The refractivity, R_L, for 546·1 mμ of CO_2 is const. to within 0·1% at 15—400°, but between 400° and 800° there is a rise of ~0·6%, which is ascribed to the thermal excitation of higher vibrational states in the mol. With AcOH at 120—300° R_L falls with rising temp., and the effect on it of *d* and temp. indicates that the fall is due to dissociation of the double mols. Association to double mols. increases R_L by ~1·5%. This increase may be due to increase in the probabilities of electron transition owing to mutual perturbation of the mols. in the complexes, and to the electron frequency determining R_L depending on the ionisation energy of the mol., which has been shown to fall on association. R. C.

Change in refractivity and dispersion on transition from the vapour to the liquid state. P. HÖLEMANN (Z. physikal. Chem., 1936, **B**, **32**, 353—368).—The mol. refractivity, R_L, of liquid $SiCl_4$, $SnCl_4$, and $SnBr_4$ at λλ 486·1, 587·6, and 656·3 mμ are represented by the dispersion formula $R_L = R_\infty\lambda^2/(\lambda^2-\lambda_0^2)$. R_L is smaller for the liquid than for the vapour state by an amount ΔR which shows no clear parallelism with the dipole moment but increases in the order $CCl_4 < SiCl_4 < SnCl_4 < SnBr_4$. A similar effect for other compounds is shown by existing data. This change in R_L is best explained by supposing it to result from the superimposition of two effects: association in the liquid state, causing a rise in R_L and deviation of the internal field in the liquid from the Lorentz–Lorenz internal field, causing a fall in R_L. With H_2O a third at most of ΔR can be explained by increase on condensation of the effect of the infra-red absorption bands on the refraction in the visible. On condensation R_∞ and λ_0 also fall. R. C.

Decrease in refraction of electrolyte solutions. T. NEUGEBAUER (Z. Physik, 1936, **99**, 677—687).—Theoretical. Changes in refraction of an electrolyte solution are not due to Debye effects, but to true association. A. B. D. C.

Anisotropy of the optical polarisation field in liquids. III. B. S. R. RAO (Proc. Indian Acad. Sci., 1936, **3**, **A**, 369—376).—The mol. refractivity of $PhNO_2$ increases with temp., and for H_2O diminishes slightly; for AcOH and HCO_2H it increases to a certain temp. and then diminishes. The coeffs. of anisotropy of the optical polarisation field are calc. for AcOH and $PhNO_2$. In the former, the polarisation field becomes more anisotropic, and in the latter, more isotropic, with rising temp. N. M. B.

Variation of double refraction in celluloid with the amount of permanent stretch at constant temperature and at different temperatures. F. C. HARRIS and B. R. SETH (Proc. Physical Soc., 1936, **48**, 477—487).—Residual double refraction was measured at const. temp. at a no. of λλ in the visible spectrum for specimens of celluloid subject to different amounts of permanent stretch by stretching beyond the elastic limit. Dispersion followed the law $n/\lambda^2 = A - B\lambda$, where n is the permanent double refraction at λ and A and B are consts. n had a max. for some val. λ_m, the vals. of λ_m increasing with permanent stretch. Temp. effects on dispersion and on λ_m were investigated. N. M. B.

Dispersion of magnetic rotation of liquid mixtures. H. POLTZ (Z. physikal. Chem., 1936, **B**, **32**, 243—273; cf. A., 1932, 678).—It is deduced theoretically that $\varphi = M[\omega]n\lambda^2/(n^2+2)^2$, where $M[\omega]$ is the mol. magnetic rotation, should have properties similar to those of the mol. refractive power, R_L, *e.g.*, should obey the mixture rule. $[\omega]$ in the visible and ultra-violet, n in the visible, and *d* have been measured for eight binary mixture over the whole concn. range. $M[\omega]$ is additive primarily in mixtures with large association complexes or without sp. intermol. effects, whilst φ approximates to additivity most closely in non-associated mixtures. In general, R_L runs parallel with φ, and R_G with $M[\omega]$, in mixtures. R. C.

Kerr effect in polar molecules. O. SPECCHIA and N. DALLAPORTA (Nuovo Cim., 1935, [ii], **12**, 15—25; Chem. Zentr., 1935, ii, 1316).—The Kerr const. for castor oil has been determined at 21°, and an expression derived for its variation with temp. J. S. A.

Maxwell effect in liquids. G. G. PALDHIKAR (Phil. Mag., 1936, [vii], **21**, 1125—1130).—An expression is derived for the Maxwell const. which is in accord with experimental data on the birefringence in state of viscous flow for 4 paraffins and 9 aromatic compounds. J. W. S.

Uses of the polar molecule concept in elementary chemistry. S. J. FRENCH (J. Chem. Educ., 1936, **13**, 122—130). L. S. T.

Structure of the formate ion. P. A. SMALL and J. H. WOLFENDEN (Nature, 1936, **137**, 781).—A criticism (cf. this vol., 663). The slowness of the exchange process between the formate ion and D_2O does not support the views of Rây and Sarkar (*loc. cit.*). With HCO_2K in neutral solution 8% exchange occurs in 8 days at 100°; the exchange is accelerated in presence of alkali. L. S. T.

Electronic theory of organic chemistry. V. Relations between the structure, reaction capacity, and polymerisation of organic compounds. V. RASUMOVSKI (Bull. Soc. chim., 1936, [v], **3**, 798—817).—A discussion. E. S. H.

Orbital valency and directed properties in the theory of the chemical linking. I, II. G. Nordheim-Pöschl (Ann. Physik, 1936, [v], 26, 258—280, 281—307).—An extension of the Heitler–London theory. Ground states of diat. mols., models of polyat. mols., theory of energy of combination, and double linkings are considered. A. J. M.

Metallic binding. I. P. Gombas (Z. Physik, 1936, 99, 729—742).—Statistical methods, applied to a lattice of positive ions surrounded by an electron gas, explain absence of conductivity from solid H_2, and give good vals. for the lattice const., lattice energy, heat of sublimation, and compressibility of K. A. B. D. C.

Metallic binding according to the combined approximation procedure. H. Hellmann and W. Kassatotschkin (J. Chem. Physics, 1936, 4, 324—325; cf. A., 1935, 278, 1058).—Calc. vals. for heats of sublimation and d_0 are in satisfactory agreement with experimental data for Na, K, Rb, and Cs. L. J. J.

Wave-mechanical treatment of the LiH molecule. J. K. Knipp (J. Chem. Physics, 1936, 4, 300—307). Theoretical. L. J. J.

Rotation–vibration wave equation for a polyatomic molecule. M. Eliashevitsch (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 295—298).—Mathematical. A. J. M.

Mechanism of addition to double linkings. III. Molecular forces between benzoquinone and *cyclo*pentadiene. A. Wassermann (J.C.S., 1936, 432—436).—London's approximation formula, $\epsilon_{kl} = 3/2 \times P_k P_l/R^6 \times \Delta E_k \times \Delta E_l/(\Delta E_k + \Delta E_l)$ ($R =$ distance between mols. k and l) for the attraction energy for simple mols. due to the "dispersion effect" (A., 1930, 1239; 1931, 149) is extended to calculate energies between large org. mols. From μ of C:O and C:C linkings, vals. of polarisability P are calc., and ΔE for the conjugated double linking from an absorption band at 2400 A. in benzoquinone (I) vapour. The lattice energy between mols. of the (I) lattice is 14·6 kg.-cal. per mol. Neglecting kinetic energy of the crystal and repulsive forces between mols., this should approximate to heat of sublimation (published val., 15 kg.-cal. per mol.). Lattice energy calc. on dipole and dipole-induction energy alone is only 7 kg.-cal. per mol. Similarly, attraction energies (due to dispersion effect) between (I) and *cyclo*pentadiene in configurations suitable for (*a*) 1 : 2-, (*b*) *exo*-1 : 4-, and (*c*) *endo*-1 : 4-addition are calc. The val. is 9—10 kg.-cal. greater for (*c*) than for (*a*). Vals. are compared with the dipole-induction energies (cf. *loc. cit.*). E. W. W.

Binding energies of molecular compounds of mono- and di-phenyl-polyene- and -polyine hydrocarbons with *s*-trinitrobenzene, and physical nature of secondary valency forces. G. Briegleb and J. Kambeitz (Z. physikal. Chem., 1936, B, 32, 305—333; cf. this vol., 410).—In dil. solutions in indifferent solvents compound formation occurs in the ratio 1 : 1. The binding energies, E, have been determined by an optical method. The results are in harmony with Hückel's theory of the polar structure of unsaturated aromatic systems (A., 1932, 901). The NO_2-compound (I) adds itself to one Ph nucleus of the hydrocarbon so that the nuclear plane of the latter is parallel to the plane of the ring of (I) and polarises the localised single σ-linkings and the *p*-electron cloud of the Ph nucleus. If in a monophenyl hydrocarbon the Ph nucleus or in a Ph_2 hydrocarbon both Ph nuclei are conjugated with a continuously conjugated chain of double or triple linkings the perturbation caused by addition of the polar component in the *p*-electron cloud of one Ph nucleus and at first localised is transmitted over the whole mol., and E is comparatively high. Such transmission is prevented by interrupting the conjugation of the Ph nucleus with the conjugated aliphatic chain by interposition of a CH_2 group; an abrupt fall in E results. There is a parallelism between the effects of constitution on the optical properties of certain mono- and di-phenyl hydrocarbons and on the E of their compounds with (I). R. C.

Direct transmission of vibrational energy from one gas molecule to another on collision. F. Patat and E. Bartholomé (Z. physikal. Chem., 1936, B, 32, 396—406).—Comparison of existing data derived from measurements of sound dispersion and absorption for the frequency with which a mol. loses a vibrational quantum on collision with data for the stabilising action of gases on $Br + Br \rightarrow Br_2$ suggests that the direct transmission of vibrational energy from one mol. to another on collision plays an important part in reaction kinetics. In unimol. decomp. this appears to be the decisive type of energy exchange and occurs at practically every collision. R. C.

Polarisation of hydrogen halides. C. H. D. Clark (Proc. Leeds Phil. Soc., 1936, 3, 208—217; cf. A., 1935, 569).—Polarisation data for H halides confirm that polarisability (α) ∝ (internuclear distance)^3. The depression of α by a proton entering a halogen ion varies linearly with the Debye "apparent polarisability" of the halide. The vals. of the dielectric consts., n_∞, dipole moments, dipole distances, α, deviation from additivity of inter-nuclear distance and mol. refraction, and the total, electron, and orientation polarisations of HF, HCl, HBr, and HI are calc. and related to the structures of the mols. The nature of the polarisation of element no. 85 is predicted. J. W. S.

Relation between polarisability and internuclear distance for simple di-atoms. F. R. Goss (Proc. Leeds Phil. Soc., 1936, 3, 231—234).—The polarisability of simple di-atoms is $kr_e^3/2$ for H_2, $(k-n/4)r_e^3$ for the KK period, and $(k+0{\cdot}20-n/4)r_e^3$ for higher periods, where $k=3{\cdot}85$ and n is the mol. group no. (cf. Clark, A., 1934, 476). J. W. S.

Molecular constants and potential energy curves for diatomic molecules. II. M. L. Huggins (J. Chem. Physics, 1936, 4, 308—312; cf. A., 1935, 1193).—Theoretical. The potential energy expression already employed is applied to diat. mols. containing heavier atoms. Calc. vals. of the equilibrium distance (r_e) generally agree with experimental vals. L. J. J.

Spectroscopy and valency. IV. Periodic groups of hydride di-atoms. C. H. D. Clark.

V. Periodic functions of hydride di-atoms. C. H. D. Clark and J. L. Stoves (Proc. Leeds Phil. Soc., 1936, **3**, 218—220, 221—230; cf. A., 1935, 432).—IV. Hydride di-atoms are classified into periodic groups according to electron configurations. It is improbable that the normal ground state spin of a diat. hydride is $>$ 1 quantum unit.

V. The spectroscopic and bond consts. of hydride di-atoms plotted against the periodic group no. of the elements show no max. as found with non-hydride di-atoms. Hydrides of elements with 18 electrons within the valency group give characteristic curves distinct from those of inert gas structure in that min. are found at group III. J. W. S.

Vibration–rotation energy levels of polyatomic molecules. II. Perturbations due to neighbouring vibrational states. E. B. Wilson, jun. (J. Chem. Physics, 1936, **4**, 313—316; cf. this vol., 667).—Mathematical. L. J. J.

Rotation of polyatomic molecules. E. Bartholomé (Z. Elektrochem., 1936, **42**, 341—359).—A review.

Characteristic vibrations of mechanical molecular models. III. Plane six-membered ring and its derivatives. F. Trenkler (Physikal. Z., 1936, **37**, 338—345; cf. A., 1935, 432, 918).—The characteristic frequencies and vibrational forms of mechanical models representing unsaturated six-membered rings (*cyclo*hexene, 1 : 3- and 1 : 4-*cyclo*hexadiene, 1 : 3 : 5-*cyclo*hexatriene, and C_6H_6) and mono- and di-derivatives of C_6H_6 agree with those expected from theory. The type of vibration is almost independent of the no. and position of the double linkings. It was not possible to observe all the theoretical vibrations of tri-derivatives of C_6H_6 and some of these deviate from theory. A. J. M.

Parachor and chemical constitution. V. Structure of liquid crystals. S. K. Ray (J. Indian Chem. Soc., 1936, **13**, 194—197).—The parachors of liquid crystals of *p*-azoxy-anisole and -phenetole and *p*-methoxybenzylideneazine at first diminish with rise of temp., then rise suddenly by 12—14 units to the val. corresponding with the true m.p., after which the increases are gradual. This irregularity is explained on the assumption that 7 or 8 mols. are associated to form a complex mol., and rise of temp. breaks down the lateral cohesion between them. C. R. H.

Parachors of methyl and ethyl nitrites and of nitromethane and nitroethane. W. A. Noyes and B. Singh (J. Amer. Chem. Soc., 1936, **58**, 802—803).—The parachors of MeONO and EtONO agree closely with those of $MeNO_2$ and $EtNO_2$. A hypothesis to explain the increase in parachor caused by a double covalency is advanced. E. S. H.

Production of clear crystal diagrams in Quenstedt linear projection by means of γ-ray interference. H. Seeman (Physikal. Z., 1936, **37**, 345—347).—The production of γ-ray interference diagrams from rock-salt is described. The result is a Quenstedt projection of the lattice. A. J. M.

Theory of the reflexion of *X*-rays by crystals. C. Mauguin (Compt. rend., 1936, **202**, 1375—1377).—Mathematical. R. S.

Numerical method for two-dimensional Fourier synthesis. C. A. Beevers and H. Lipson (Nature, 1936, **137**, 825—826). L. S. T.

Lattice constants for 1936. M. C. Neuburger (Z. Krist., 1936, **93**, 1—36).—Tables give the best accepted figures for the lattice consts. of the elements, with their lattice types, *d*, at. wt., vol. occupied by the atom, distance of nearest neighbours, etc. References to the literature are given, and data as to the purity of the specimens measured. B. W. R.

Complete fibre diagrams. E. Sauter (Z. Krist., 1936, **93**, 93—106).—For obtaining the fullest information about fibre structure from *X*-rays there are advantages in using a conical film with axis parallel to the fibre axis. A camera suitable for such photographs is described, and examples of its use are given. The interpretation of the photographs is as simple as for the usual type. B. W. R.

Relation between faults and growth-cessations in crystals. E. Herlinger (Z. Krist., 1936, **92**, 372—379).—The occurrence of a fault in a crystal growth causes a disturbance of the lattice field which may eventually introduce further faults. The process is traced in detail; alterations of habit and of growth rate may be due to this cause. B. W. R.

Structure of the real macro-crystal. E. Herlinger (Z. Krist., 1936, **92**, 380—386).—Further consequences of the effects of faults, resulting in diminished energy of the surface of an irregular crystal as compared with that of the ideal crystal (cf. preceding abstract), are considered. B. W. R.

Technique for the construction of models illustrating the arrangement and packing of atoms in crystals. M. J. Buerger and R. D. Butler (Amer. Min., 1936, **21**, 150—172). L. S. T.

Statistical theory of superlattices with unequal concentrations of the components. R. Peierls (Proc. Roy. Soc., 1936, *A*, **154**, 207—222).—Bethe's method (A., 1935, 1193) is generalised to include a cubic face-centred lattice of composition AB_3 (*e.g.*, $AuCu_3$). L. L. B.

Influence of the symmetry of the medium on the symmetry of corrosion figures in crystals. L. Royer (Compt. rend., 1936, **202**, 1346—1348; A., 1930, 21).—Definite corrosion figures were obtained from cryst. apatite and wulfenite with org. acids. Active and inactive acids (*e.g.*, the tartaric acids) gave different and characteristic figures. The effect depends on the symmetry of the crystal and on that of the solution. H. J. E.

Photometric measurement of the number of oriented crystallites in metallic wires. J. G. de la Cueva (Anal. Fís. Quím., 1935, **33**, 433—437).—The Debye–Scherrer method can be adapted to the determination of the proportion of oriented crystallites in drawn Al wire. There is an increase from 51·72% for 1·78 mm. to 80% for 0·58 mm. diameter wire. The permanent residue of unoriented crystallites is considered to occur in the surface layer and to be produced by friction during the drawing of the wire. F. R. G.

***X*-Ray study of the electrolytic deposition of cadmium.** A. Rubio and J. G. de la Cueva (Anal. Fís. Quím., 1935, **33**, 521—532).—Cd deposited from a solution (1 litre) of CdO 39·4 g., KCN 128·2 g., Na_2SO_4 50·0 g., and $NiSO_4$ 1·0 g. with or without addition of colloid has a grain $> 10^{-6}$ cm. The lattice consts. are identical with those of ordinary Cd and the plane $(11\bar{2}2)$ is oriented parallel to the plane of the sample. The influence of c.d., the nature of the cathode, and the presence of colloid on the orientation of the crystals is discussed. F. R. G.

To what class of symmetry does ordinary ice belong ? N. Seljakov (Compt. rend. Acad. Sci. U.R.S.S., 1936, **1**, 293—294).—*X*-Ray analysis of ice by the Laue method shows the existence of α- and β-ice. The former belongs to one of the classes D_{6h}, D_6, C_{6v}, and D_{3h} (hexagonal ice), and the latter to one of the classes C_{3i} and C_3 (rhombohedral ice). Both modifications are stable. α-Ice is formed when the temp. of the surrounding air is a little $< 0°$, and β-ice at lower temp. A. J. M.

Morphological and structural relations in cuprite. W. Kleber and R. Schroeder (Neues Jahrb. Min., 1935, **A**, 69, 364—387; Chem. Zentr., 1935, ii, 1326).—From a review of the relevant crystallographic, optical, and *X*-ray data, cuprite is allocated to the space-group O^2 of the trioctahedral crystal class. J. S. A.

Structure of α-quartz. P. H. Wei (Z. Krist., 1936, **92**, 355—362).—Parameters for the already known structure are determined from intensity measurements. Primary extinction in the crystal is measured by abs. methods, and is considerable. B. W. R.

Structure of strontium and barium peroxides, SrO_2 and BaO_2. J. D. Bernal, E. Djatlova, I. Karsanovski, S. Reichstein, and A. G. Ward (Z. Krist., 1936, **92**, 344—354).—The structures are of the CaC_2 type, a_0 5·02 c_0 6·55 and a_0 5·34 c_0 6·77 A., respectively. Space-group *F*4/*mmm*. The parameters are determined. The distance O–O is found to be 1·31 A. B. W. R.

Lattice constant of galena with new Röntgen spectrometer. E. von Zeipel (Ark. Mat. Astron. Fysik, 1935, **25**, **A**, No. 8; Chem. Zentr., 1935, ii, 1326).—From precision measurements by a substitution method on a new type of instrument (described), using Ag $K\alpha_1$ radiation in the first 4 orders, $2d=5923{\cdot}34$ X. The half-val. width of the Ag $K\alpha_1$ line$=5{\cdot}6''$. J. S. A.

Rotation of anionic polyhedra in cubic crystal lattices. II. Borofluorides. C. Finbak and O. Hassel (Z. physikal. Chem., 1936, **B**, **32**, 433—438).—The *X*-ray diagrams of the cubic high-temp. forms of NH_4BF_4 and KBF_4 point to a rotation of the anion as in perchlorates (cf. this vol., 669). In the transformation of $KClO_4$ and NH_4BF_4 from the rhombic into the cubic form the occurrence of the displacement of anions and cations postulated by Herrmann and Ilge (A., 1931, 414) has been demonstrated. In the rotation of anions there will be resonance between this rotation and the directed oscillation of the cations. In cubic KPF_6, NH_4PF_6, and $TlPF_6$ there is rotation of the $PF_6{}'$ ions. R. C.

Crystal structure of radium fluoride. G. E. R. Schulze (Z. physikal. Chem., 1936, **B**, **32**, 430—432).—RaF_2 crystallises in the fluorspar lattice with *a* 6·368 A. and *d* 6·75. The radius of Ra¨ for co-ordination no. 6 is 1·52 A. R. C.

Configuration of the azide ion. L. K. Frevel (J. Amer. Chem. Soc., 1936, **58**, 779—782).—The N–N distances in crystals of NaN_3 and KN_3 have been determined by the *X*-ray method as 1·150±0·016 and 1·145±0·017 A., respectively. In NH_4N_3 it is 1·165±0·021 A. E. S. H.

Space-group of calcium sulphate dihydrate. J. Palacios and L. Rivoir (Anal. Fís. Quím., 1935, **33**, 518—520).—A re-examination of the crystal structure of gypsum (cf. A., 1930, 139) shows that, contrary to Onorato (A., 1930, 672), the space-group is C_{2h}^6. F. R. G.

Structure of some hydrates of sodium borate. W. Minder (Z. Krist., 1936, **92**, 301—309).—Cell consts. and space-groups of the following compounds are determined: kernite $Na_2B_4O_7,4H_2O$, tinkalconite $Na_2B_4O_7,5H_2O$, borax $Na_2B_4O_7,10H_2O$. The results are discussed in relation to the effective vol. occupied by the additional H_2O. B. W. R.

Crystal structure of silver phosphate. L. Helmholz (J. Chem. Physics, 1936, **4**, 316—322).—Laue and oscillation diagrams of Ag_3PO_4 give 5·995 A. for the edge of the cubic unit containing two mols. The space-group is T_d^4. A new val. for the O parameter has been obtained, giving P–O in :PO_3 1·61±0·03 A. The discrepancy with KH_2PO_4 is due to covalent bond formation of O with Ag atoms, which must be treated as oscillators with tetragonal symmetry. The ratio of the amplitudes of vibration along and perpendicular to the tetragonal axis is calc. L. J. J.

Crystal structure of barium antimonate. J. Beintema (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 652—661).—$Ba(SbO_3)_2,8H_2O$ forms monoclinic prismatic (pseudo-orthorhombic) crystals (a_0 9·961, b_0 12·506, c_0 10·129 A.; β 87° 17′; 1 mol. in unit cell; space-group C_{2h}^6). The Sb atoms are arranged in layers perpendicular to the *b* axis. The distance between such layers is 6·253 A. The distance between Sb atoms in a layer is approx. 5 A. Each Sb is surrounded by 6 O atoms, forming $\{Sb(OH)_6\}'$. The composition is $Ba\{Sb(OH)_6\}_2,2H_2O$. H. J. E.

Crystallography of lithium molybdotellurate. J. D. H. Donnay and J. Mélon (Amer. Min., 1936, **21**, 125—127).—$3Li_2O,TeO_3,6MoO_3,13H_2O$, *d* 2·2±0·1, hardness 2½, rhombohedral-hexagonal, uniaxial negative, n_ϵ 1·612, n_ω 1·703 (both ±0·001) for Na light. L. S. T.

Crystal structure of hexaethylbenzene. H. K. Pal and A. C. Guha (Z. Krist., 1936, **92**, 392—394).—Goniometric measurements are given; the cell is triclinic with a_0 9·90, b_0 9·84, c_0 6·10 A., α 58° 5′, β 103° 54′, γ 123° 43′. B. W. R.

Magnetic isotropy and crystal structure of hexaethylbenzene. N. Ganguli (Z. Krist., 1936, **93**, 42—46).—Magnetic measurements on single crystals are used to locate an approx. plane of magnetic symmetry, parallel to which the C_6 rings of the mols. should lie. B. W. R.

Molecular structure of quinhydrone. J. Palacios and O. R. Foz (Anal. Fís. Quím., 1935, **33**, 627—642).—Contrary to the authors' earlier work (A., 1932, 904), quinhydrone (I) crystals are triclinic, pseudomonoclinic, pseudorhombic, and pseudohexagonal; space-group C_2; *a* 21·8, *b* 6·04, *c* 7·70 A.; they exhibit a subperiodicity due to alternation of mols. of benzoquinone (II) and quinol (III). Vals. of $\chi_m \times 10^6$ are (I) $-84{\cdot}2_3$, (II) $-33{\cdot}3_1$, (III) $-64{\cdot}5_8$. (I) does not exist as a free radical. F. R. G.

***X*-Ray analysis of the dibenzyl series. III. Structure of stilbene, tolane, and azobenzene.** J. M. Robertson, M. Prasad, and (Miss) I. Woodward (Proc. Roy. Soc., 1936, **A**, **154**, 187—195; cf. A., 1933, 1107).—Detailed measurements have been made on stilbene, and sufficient preliminary data obtained for tolane and azobenzene to show that the three structures are closely similar. The space-group is C_{2h}^5 ($P2_1/a$), with 4 mols. per unit cell. In stilbene, the 4 mols. have centres of symmetry which coincide with 4 crystal centres; 2 of the mols. have orientations similar to that of dibenzyl, whilst the other 2 can be derived from them by a rotation of 180° about the *a* axis and a translation of ½*c*. The proposed structure is compatible with the other physical properties of the crystal, including the magnetic data. L. L. B.

Crystal structure of condensed ring compounds. I. 1 : 2-*cyclo*Pentenophenanthrene. II. 7-Methoxy-3′ : 3′-dimethyl-1 : 2-*cyclo*pentenophenanthrene and 7-methoxy-1 : 2-*cyclo*pentenophenanthrene. J. Iball (Z. Krist., 1936, **92**, 293—300; **93**, 47—56).—I. The cell is monoclinic, a_0 18·38, b_0 5·83, c_0 23·61 A., β 114·3°; *d* 1·23; 8 mols. in cell; space-group $B\ 2_{1/c}$. The reflexion intensities show marked similarities with the analogous ones from chrysene, which enables the orientation of the mols. to be determined approx.

II. Both compounds are monoclinic, space-group C_{2h}^5; cell data and optical data are given, and the probable position of the mols. in the cell is located on the basis of these data and the reflexion intensities. B. W. R.

Crystal studies on certain *p*-toluenesulphonamides. I. Nitrogen-substituted sulphonanilides. II. Nitrogen-substituted sulphon-*o*-toluidides. III. Nitrogen-substituted sulphon-*p*-toluidides. G. H. Young, W. J. Keith, and A. P. Honess (Z. Krist., 1936, **92**, 216—220, 395—401; **93**, 107—112).—I. Crystallographic data are given for *p*-toluenesulphon-*N*-*iso*propylanilide, and for the corresponding *N*-*n*- and *N*-*sec*-Bu compounds.

II. A goniometric description of *p*-toluenesulphon-*N*-methyl-*o*-toluidide and the corresponding *N*-Et, -Pr^{α}, -Pr^{β}, -Bu^{α}, -Bu^{β}, and -*iso*amyl compounds.

III. Crystallographic descriptions of *p*-toluenesulphon-*N*-methyl-*p*-toluidide and the corresponding Et, Pr^{β}, Bu^{β}, *n*- and *iso*-amyl compounds are given. B. W. R.

***X*-Ray studies on choleic acids.** Y. Go and O. Kratky (Z. Krist., 1936, **92**, 310—312).—Compounds of deoxycholic acid with the saturated fatty acids give sensibly the same *X*-ray photographs with from 3 to 22 C atoms. A typical set of photographs is analysed; the rhombic cell has a_0 25·8, b_0 13·5, c_0 7·22 A.; space-group probably V^3. B. W. R.

***X*-Ray study of myosin.** W. T. Astbury and (Mrs.) S. Dickinson (Nature, 1936, **137**, 909—910; cf. this vol., 623). L. S. T.

Experiments with models on the theory of the Kikuchi lines. A. Lichtenfeld and K. Schwarz (Naturwiss., 1936, **24**, 377).—A reply to von Laue (cf. this vol., 554). A. J. M.

Electron analysis: influence of the prolonged passage of a beam of electrons through thin films. J. J. Trillat and S. Oketani (Compt. rend., 1936, **202**, 1332—1334).—The diffraction pattern from a thin cryst. Au film disappears gradually on exposing a single spot on the film continuously to the electron beam for 1½ hr. The effect is attributed to local heating (cf. Andrade and Martindale, A., 1935, 1449). H. J. E.

Structure of thin metallic films deposited on rock-salt by vaporisation. L. Brück (Ann. Physik, 1936, [v], **26**, 233—257).—The structure of films of Ag, Au, Al, Cu, Ni, Pd, Co, Fe, and Cr deposited on NaCl by vaporisation in vac. was investigated by electron diffraction. Above a temp. characteristic of each metal, films of Au, Ag, Al, Ni, Cu, and Pd possessed a mosaic structure, the crystallites being oriented in the same direction. Fe and Cr showed three directions of orientation. The previously discovered orientation rule for substances deposited on a cryst. base holds only for deposition from solution. A. J. M.

Electron diffraction by single crystals. O. Specchia and N. Dallaporta (Nuovo Cim., 1935, [ii], **12**, 4—14; Chem. Zentr., 1935, ii, 1311).—The formation of supplementary lines and bands in the diffraction pattern is discussed. J. S. A.

Electron-diffraction study of the structure of electro-deposited metals. G. I. Finch and C. H. Sun (Trans. Faraday Soc., 1936, **32**, 852—863).—The structure of electro- and chemically deposited metal films on metallic substrates has been studied. Orientation of the substrate crystals nearly always determines that of the electro-deposit, whilst films deposited on amorphous surfaces show normal orientation. Adhesion increases with orienting effect. An anomalous double diffraction observed with composite films is discussed. Chemical displacement leads to alloy formation. L. J. J.

Diffraction of electrons by amalgam films. A. E. Aylmer, G. I. Finch, and S. Fordham (Trans. Faraday Soc., 1936, **32**, 864—871).—Extra rings due to amalgam formation on Au, Ag, Cu, and Pd leaf have been investigated. Au and Ag form simple cubic amalgams with *a* 17·81 and 17·94 A., respectively, and Ag also forms two face-centred tetragonal amalgams. Pd is partly attacked. L. J. J.

Structure of the paraffin chain studied by means of electron rays. R. Rigamonti (Gazzetta, 1936, 66, 174—182).—Electron diffraction measurements with long-chain paraffin hydrocarbons confirm the results of *X*-ray investigations. The angle between the plane of symmetry of the paraffin chain and the (010) crystal plane is calc. to be 35—50° and the C–H distance 1·25 A. These vals. are confirmed by steric considerations. O. J. W.

δ-Quartz. L. Balamuth, F. Rose, and S. L. Quimby (Physical Rev., 1936, [ii], **49**, 703).—Quartz can be piezoelectrically excited at a temp. as low as 78° abs., contrary to Osterberg's result (cf. this vol., 672). N. M. B.

Changes in magnetisation of nickel and permalloy and of nickel–iron crystals in high fields. G. Gerloff (Z. Physik, 1936, **99**, 585—594).—The susceptibility of Ni and permalloy attains a const. end val. at 4000 gauss, changing by $<6\%$ up to 5500 gauss. A. B. D. C.

Conditions of demagnetisation of rhombohedral iron sesquioxide. A. Michel (Compt. rend., 1936, **202**, 1769—1771; cf. A., 1935, 1063).—Pptd. Fe_2O_3, annealed at 700°, shows a rapid increase in magnetisation above 600° (anomaly *A*). On cooling again the magnetisation rises normally with decrease of temp. to below the Curie point, then attains a max., decreases slightly (anomaly *a*) and thereafter remains approx. const. to room temp. On annealing at 800—900°, *A* occurs at 560°, whilst *a* disappears, but after annealing above 1000°, *A* is still lower. After annealing for several hr. at 1300°, normal reversible magnetisation curves are obtained. The min. temp. of demagnetisation of annealed Fe_2O_3 can occur below the Curie point, but it is always above the temp. of anomaly *a*. J. W. S.

Temperature variation of electron spin paramagnetism. E. C. Stoner (Proc. Leeds Phil. Soc., 1936, **3**, 191—199).—Expressions are derived for the temp. variation of paramagnetic susceptibility due to electron spin. The bearing of the results on the magnetic properties of metals is discussed. J. W. S.

Total reflecting power as a function of temperature in the neighbourhood of the Curie point. L. S. Ornstein and J. H. van der Veen (Physica, 1936, **3**, 289—300).—The total reflecting power of Fe for λ 6500 A. and angle of incidence about 15° rises rapidly and continuously from about 62% to 66% when the temp. rises from 1000° to 1100° abs. It is concluded that the internal magnetic field does not disappear abruptly at the Curie point, but some remains up to 1100°. It is suggested that the Curie point for some regions of spontaneous magnetisation is a function of the orientation of the internal field towards the crystal lattice of this region. No large change in reflecting power occurs at the β–γ transition point (1180° abs.). J. W. S.

Variation of Young's modulus with magnetisation and temperature in nickel. S. Siegel and S. L. Quimby (Physical Rev., 1936, [ii], **49**, 663—670).—For annealed polycryst. Ni, 99·7% pure, the % increase in Young's modulus, $E, \propto J^2$ ($J=$ intensity of magnetisation) over 0—0·4 saturation at all temp. below 311°. The total increase in *E* from the demagnetised to the saturated state is 6·7% at 23°, reaching a max. of 18·7% at 185°, and decreasing to zero at the Curie point. Results are in general agreement with Akulov's theory (cf. A., 1933, 1237). N. M. B.

Plasticity of bismuth crystals. H. J. Gough and H. L. Cox (Nature, 1936, **137**, 701).—Photomicrographs of Bi crystals showing deformation by " slip " following compression are reproduced. Deformation by twinning is more common. L. S. T.

Dependence of plasticity on temperature. H. Ekstein (Z. Krist., 1936, **92**, 253—274).—The elastic properties of W single crystals at −185° and 16°, of rock-salt over the range 300° to −250°, and of bakelite over the range 16° to 60° have been measured. Agreeing with previous results on cryst. substances, the temp. variation is not sufficient to suggest that plasticity is thermal in origin; for the amorphous bakelite the very large variation of elastic consts. agrees with the temp. theory of plasticity. B. W. R.

Photo-electric method for determining the elastic limit of an *X*-rayed rock-salt crystal. M. N. Podaschevski (Physikal. Z. Sovietunion, 1935, **7**, 399—409). Ch. Abs. (*e*)

Statistical molecular configuration and elastic properties of substances of high mol. wt. W. Kuhn (Naturwiss., 1936, **24**, 346—347).—Theoretical. A. J. M.

Elastic constants, electrical resistance, and thermal expansion of magnesium crystals. E. Goens and E. Schmid (Physikal. Z., 1936, **37**, 385—391).—The principal elastic consts., sp. resistance at room temp., relative electrical resistance over the temp. range −269° to 100°, and the principal vals. of the thermal expansion over the range −253° to 200° have been determined for single hexagonal Mg crystals for different crystallographic orientations. The anisotropy of these physical properties, though < that for Zn and Cd, is > would be expected considering the close resemblance of the Mg lattice to the hexagonal close-packed lattice. A. J. M.

Principal elastic constants of single crystals of copper, gold, and lead. E. Goens (Physikal. Z., 1936, **37**, 321—326).—The vals. of the principal elastic consts., S_{11}, S_{12}, S_{44}, of single crystals of Cu, Au, and Pb, obtained by a dynamic method, were Cu, 14·91, −6·25, 13·28, respectively, Au, 23·30, −10·65, 23·80, respectively, and Pb, 93·0, −42·6, 69·4, respectively (all $\times 10^{-13}$ sq. cm. per dyne). The corresponding principal elastic moduli, C_{11}, C_{12}, and C_{44} were also calc. The Cauchy relation ($C_{12}=C_{44}$) is not satisfied. The results for Cu do not agree with those of Kimura (A., 1933, 1237). A. J. M.

State of electrolytically separated metals. G. Tammann and H. Jaacks (Z. anorg. Chem., 1936, **227**, 249—260).—Electrolytically separated metals, *e.g.*, Cu, Fe, Zn, and Ni, have a hardness similar to that of cold-worked metal, and, in both cases, the structure is fibrous. The fibres are formed perpendicular to the cathode. The reflected Co K_a line shows an increased sharpness of the interference lines on heating in all cases except Cu. The metals may contain considerable quantities of H_2, which is removed by heat, but this appears to bear no relation to the hardness. The H_2 content varies in the different layers of the electrolytic metal, causing scaling. The rate of dissolution of electrolytic Fe in acids varies with the treatment, the untreated Fe being less readily attacked than the fused or milled metal. The rate for electrolytic Zn is not much affected by treatment. The temp. of separation of a metal greatly affects polarisation. M. S. B.

Orientation of oxide films on iron. R. F. Mehl and E. L. McCandless (Nature, 1936, **137**, 702; A., 1935, 161).—*X*-Ray photographs of FeO films on single crystals of Fe show reflexions from Fe_3O_4 resulting from partial decomp. of the wüstite phase. The Fe_3O_4 is identically oriented with the FeO with all planes of the same indices in the two cubic lattices parallel. The same orientation relationship holds when an FeO film is grown by reduction on a natural crystal of magnetite. The Fe atoms determine the orientation relationship in the case of FeO on Fe and the oxygen atoms that of Fe_2O_3 on Fe_3O_4. L. S. T.

Isomorphism of organic compounds. H. Lettré, H. Barnbeck, and W. Lege (Ber., 1936, **69**, [*B*], 1151—1154).—Investigation of the systems from the hydroxy-, chloro-, and methyl-benzoic acids taken in corresponding pairs, of r-$OH\cdot CHPh\cdot CO_2H$ and r-$CHClPh\cdot CO_2H$, and of cholesterol and cholesteryl chloride combined with the results of Grimm (A., 1931, 1363) shows isomorphous replaceability between OH and Me in one of five cases, of OH and Cl in four of 12 cases, and of Cl and Me in six of nine instances examined. Formation of mixed crystals is not observed in the systems: stilbene–phenanthrene (I), $(CH_2Ph)_2$–(I), $CHPh\colon CPh_2$–benzylidenefluorene, C_2Ph_4–9 : 10-diphenylphenanthrene. H. W.

Application of the theory of thermal oscillations to the field of mesophases (liquid crystals). H. Zocher (Kolloid-Z., 1936, **75**, 161—163).—Theoretical. E. S. H.

Mol.-wt. changes of sulphur monochloride. W. A. Patrick and N. Hackerman (J. Physical Chem., 1936, **40**, 679—688).—Determinations in a modified Cottrell b.-p. apparatus, using C_6H_6, CCl_4, $CHCl_3$, *cyclo*hexane, and PhMe as solvents, show that the mol. wt. of S_2Cl_2 is affected by its age, temp., solvent, and concn. The abnormal vals. are assumed to be due to the presence of a polymeride $(S_2Cl_2)_2$, which breaks up into S_8 and S_2Cl_4. The change with concn. is also due to equilibrium between large and small mols. of S. E. S. H.

Mol. wt. of fused yellow phosphorus. N. D. Litvinov (J. Appl. Chem. Russ., 1936, 9, 589—590).—The mol. wt. corresponds with P_4 at 50—95°. R. T.

Phenomenological theory of superconductivity. E. Schrödinger (Nature, 1936, **137**, 824).—London's theory (A., 1935, 689) is simplified. L. S. T.

Conductance of salt crystals. W. Jost (J. Chem. Physics, 1936, 4, 323).—A reply to Rodebush and Cooke (this vol., 138). L. J. J.

Magnetic anisotropy of resorcinol. K. Lonsdale (Nature, 1936, **137**, 826).—Measurements of the diamagnetic anisotropy of a single crystal of resorcinol are recorded. The derived orientation of the mol. plane relative to the crystal axes agrees with the results of a Fourier analysis. L. S. T.

Appearance of ferromagnetism in some paramagnetic salts at very low temperatures. M. Kürti, P. Lainé, B. V. Rollin, and F. Simon (Compt. rend., 1936, **202**, 1576—1578).—NH_4 Fe alum behaves as a ferromagnetic substance at approx. 0·01° abs. H. J. E.

Diamagnetic susceptibility of heavy water. V. C. G. Trew and J. F. Spencer (Nature, 1936, **137**, 706).—Using a modified Gouy balance, the mass susceptibility obtained for 99·2% D_2O, d 1·1049, is $0{\cdot}637\pm0{\cdot}001\times10^{-6}$ unit at 20° (cf. this vol., 672), H_2O being $0{\cdot}720\times10^{-6}$. L. S. T.

Magnetic susceptibility of chlorine hexoxide. J. Farquharson, C. F. Goodeve, and F. D. Richardson (Trans. Faraday Soc., 1936, **32**, 790—795).—The magnetic susceptibility of solid and liquid Cl_2O_6 has been measured between −40° and 10°. The % of ClO_3 present at various temp., and the corresponding equilibrium consts., have been calc. by using theoretical vals. for Cl_2O_6 and ClO_3. The heat of dissociation is calc. to be 1730 ± 500 g.-cal. per mol. $d^{3\cdot5}=2{\cdot}023\pm0{\cdot}003$; coeff. of cubical expansion$=12\pm3\times10^{-4}$. F. L. U.

Magnetochemical studies. XXI. Molybdenum and tungsten halides. Magnetic behaviour of compounds of the higher transitional elements. W. Klemm and H. Steinberg (Z. anorg. Chem., 1936, **227**, 193—213; cf. this vol., 556).—Susceptibilities of $MoCl_3$, $MoCl_5$, $MoBr_3$, $MoBr_4$, WCl_2, WCl_5, WCl_6, and WBr_5 have been determined at 20°, −78°, and −183°. F. L. U.

Magnetic study of mixed crystals of bivalent copper and silver. L. Capatos and N. Perakis (Compt. rend., 1936, **202**, 1773—1775).—$[Ag^{II},4C_5H_5N]S_2O_8$ and $[Cu^{II},4C_5H_5N]S_2O_8$ have magnetic moments of 9·11 and 9·78 Weiss magnetons, respectively. Study of mixed crystals of these compounds shows that addition of small amounts of either compound to the other lowers the Curie const., but that a max. is attained at about equimol. concns. The Curie points change in parallel manner. J. W. S.

Magnetochemical investigations. XXII. Magnetic behaviour of chromium–phenyl compounds. W. Klemm and (Frl.) A. Neuber (Z. anorg. Chem., 1936, **227**, 261—271).—The magnetic moment of Hein's Cr–Ph compounds (A., 1931, 1435) is approx. 1·73 Bohr magnetons, whether the compound contains 5, 4, or 3 Ph per Cr. It is concluded that Cr^{V} is present in all cases. Formulæ are discussed. M. S. B.

[Magnetic behaviour of chromium–phenyl compounds.] F. Hein (Z. anorg. Chem., 1936, **227**, 272; cf. preceding abstract).—A reference to the formulæ for Cr–Ph compounds. M. S. B.

Polymerisation and diamagnetic susceptibility. S. S. Bhatnagar, M. B. Nevgi, and R. N.

MATHUR (Z. Physik, 1936, **100**, 141—144).—Polymerisation of anthracene, $COMe_2$, PhCHO, furfuraldehyde, and AcCN leads to a decrease in sp. diamagnetic susceptibility. A. B. D. C.

Magnetic susceptibilities of organic substances in different physical states. A. BOSE (Phil. Mag., 1936, [vii], **21**, 1119—1125).—Within limits of experimental error the diamagnetic susceptibilities of 27 org. compounds investigated are independent of their physical state (single crystal, molten liquid, or solution). J. W. S.

Magnetic properties of superconductors. T. C. KEELEY and K. MENDELSSOHN (Proc. Roy. Soc., 1936, A, **154**, 378—385; cf. A., 1935, 1309).—Previous experiments have been extended to a greater no. of superconducting substances, the specimens used being in the form of long rods in a longitudinal field. The change from superconductivity to the normal state takes place in a small temp. interval, which increases as the temp. falls. The steepness of the transition in Sn single crystals is much > in polycryst. Sn, and the transition region can be reduced further by using highly purified substances. L. L. B.

Ultrasonic velocities in liquid mixtures. S. PARTHASARATHY (Proc. Indian Acad. Sci., 1936, **3**, A, 297—303; cf. this vol., 277).—Data and graphs of ultrasonic velocities and adiabatic compressibilities are given for binary liquid mixtures of CCl_4 with C_6H_6, CS_2, EtOAc, and tetralin. The types of curve found for adiabatic compressibility–concn. are similar to those previously found for intensity of scattered light–concn. (cf. A., 1934, 1056). N. M. B.

Absorption of ultrasonic waves in liquids. J. CLAEYS, J. ERRERA, and H. SACK (Compt. rend., 1936, **202**, 1493—1494).—The absorption coeffs. of ultrasonic waves in H_2O, CCl_4, C_6H_6, CS_2, and MeOAc are > the theoretical. Addition of a small amount of CCl_4 greatly diminishes the absorption in CS_2. The deviation from the classical theory is attributed to hysteresis of the adiabatic compressibility of liquids. R. S.

Measurements of absorption, velocity, and out-gassing [of liquids] in the ultrasonic region. C. SÖRENSEN (Ann. Physik, 1936, [v], **26**, 121—137).—Data are recorded for a no. of liquids at frequencies of 194—950 kHz. Except with H_2O, the absorption increases with frequency, and with EtOH, C_6H_6, and PhMe depends on the intensity of the radiation. The energy required to expel 1 c.c. of gas from H_2O and oil at a no. of frequencies has been measured. The velocity in C_6H_6 decreases with increasing frequency. L. J. J.

Specific heats of the mineral oxides: vitreous silica, lime, alumina, as a function of temperature. A. THURET (Compt. rend., 1936, **202**, 1368—1370).—Equations in good agreement with experimental data have been deduced for the mean and the true sp. heats. R. S.

Hydrogen sulphide. Heat capacity and vapour pressure of solid and liquid. Heat of vaporisation. Comparison of thermodynamic and spectroscopic values of the entropy. W. F. GIAUQUE and R. W. BLUE (J. Amer. Chem. Soc., 1936, **58**, 831—837).—Heat capacities have been determined from 16° abs. to the b.p. A transition was observed at 103·52° abs. and a large energy absorption, possibly ending in a transition, near 126° abs. H_2S has m.p. 187·61° abs., b.p. 212·77° abs., heat of fusion 568·1 and heat of vaporisation at the b.p. 4463 g.-cal. per mol. The v.p. has been determined over the range 164·90—213·17° abs. The calc. mol. entropy of the gas at the b.p. is $46·38\pm0·1$ e.u., neglecting the nuclear spin entropy. E. S. H.

Simplified method of calculating entropy of organic compounds. I. I. STRELKOV (Ukrain. Chem. J., 1936, **11**, 32—40).—The entropy of org. compounds at 25° is given by kC, where C is the mol. sp. heat, and $k=1·1$ for solids, and 1·4 for liquids. R. T.

Changes in thermal and calorimetric values along the two fusion curves of helium. J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 612—622).—The triple point is at 1·774° abs./28·91 atm. Data for the v.p. and latent heat are recorded. H. J. E.

Latent heat of tin in passing from the superconductive to the non-superconductive state. W. H. KEESOM and P. H. VAN LAER (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 573—574, and Physica, 1936, **3**, 371—384).—The val. obtained with fields of 50—140 gauss agrees with that calc. thermodynamically. The magnetic field within the Sn was zero so long as the whole body was superconductive. In the transition range it increased gradually. H. J. E.

F.p. snd b.p. of propane. M. M. HICKS-BRUUN and J. H. BRUUN (J. Amer. Chem. Soc., 1936, **58**, 810—811).—After treatment with $ClSO_3H$ and subsequent fractional distillation, propane has f.p. $-187\pm0·1°$ and b.p. $-42·17\pm0·05°$. E. S. H.

Boiling under constant pressure. G. DUCH (J. Chim. phys., 1936, **33**, 414—426).—Approx. formulæ are derived connecting the reduced mol. attraction force $\varphi\gamma$, the surface tension A, and the mol. radius r of a liquid. For a related group of org. liquids, $\Delta\varphi\gamma/\Delta(1/r)$ and $\Delta A/\Delta(1/r)$ should be const.; this is in general supported by published or experimental vals. of the physical quantities involved. R. C. M.

Thermal properties of halides. X. Vapour pressures and vapour densities of gallium trihalides. W. FISCHER and O. JÜBERMANN (Z. anorg. Chem., 1936, **227**, 227—236).—M.-p. determinations in quartz tubes in vac. give $GaCl_3$ $77·9\pm0·2°$, $GaBr_3$ $121·5\pm0·6°$, and GaI_3 $212\pm1°$. The v.p. of the unsaturated and saturated vapours has been determined with a quartz spiral manometer and the following vals. for the b.p. have been deduced: $GaCl_3$ 201·3°, $GaBr_3$ 279° (at 750 mm.), GaI_3 346°. The degree of dissociation of Ga_2X_6 into $2GaX_3$ has been calc. at m.p. and b.p. This increases from chloride to iodide whilst the heat of dissociation diminishes and the heat of volatilisation increases. M. S. B.

Hydrocarbon vapour pressures. E. R. Cox (Ind. Eng. Chem., 1936, 28, 613—616).—V.-p. data for all hydrocarbons having mol. wt. $>$ 30 can be correlated by three equations, if b.p., crit. temp. and pressure are known, and the latter can be calc. for the normal paraffin series. H. C. M.

Phase equilibria in hydrocarbon systems. XIII. Joule–Thomson coefficients of propane. B. H. Sage, E. R. Kennedy, and W. N. Lacey (Ind. Eng. Chem., 1936, 28, 601—604).—Joule–Thomson coeffs. of pure C_3H_8 gas were determined at six temp. between 21° and 105° and at pressures up to 550 lb. per sq. in. using a small automatically maintained const.-pressure drop across a radial-flow porous plug at a given temp. and pressure, the fall in temp. of the gas in passing through the plug being measured. H. C. M.

Isotherms of ethylene between 0° and 150° and at pressures from 20 to 270 atmospheres. A. Michels, J. de Gruyter, and F. Niesen (Physica, 1936, 3, 346—351).—The isotherms have been measured at 0°, 25°, 50°, 75°, 100°, 125°, and 150°, and empirical equations for *pv*, correct to 0·01%, are calc. for the respective temp. From the $(pv_{t+12\cdot5}-pv_{t-12\cdot5})/25$—$t$ curves for different densities it is concluded that c_v increases with increasing density to pass through a max. at the crit. density. J. W. S.

Vapour pressure of mercury dimethyl. F. Ratman (J. Appl. Chem. Russ., 1936, 9, 591—593).—The v.p. is given by $\log P=6\cdot53-1050/T-11{,}000/T^2$, at −60° to 100°. R. T.

Internal changes in the system SO₃. I. A. Smits and N. F. Moerman (Z. physikal. Chem., 1936, B, 32, 369—382).—The v.p., *p*, of a specimen of α-SO_3 prepared by partial evaporation of equilibrated α-SO_3 and not in internal equilibrium increases with time according to a hyperbolic curve. Such SO_3 begins to melt only at a temp. considerably above the triple point, showing that the mass is disequilibrated throughout. On irradiation with Cu $K\alpha$ radiation *p* rises at a const. rate to a val. corresponding with the v.p. of the α-form in internal equilibrium, then remains const. It follows that *X*-rays accelerate equilibration. From measurements of the heat of mixing of molten SO_3 with 83% H_2SO_4 and the heats of dissolution in this solvent of disequilibrated and equilibrated α-SO_3 the mol. heat of fusion of a disequilibrated specimen was found to −1·8 kg.-cal., changing to −5·0 kg.-cal. after irradiation with *X*-rays. This latter val. agrees with that calc. from v.-p. data for α-SO_3 in internal equilibrium, showing that *X*-rays effect internal equilibration throughout the solid. R. C.

Thermal conductivity of deuterium. G. W. Kannuluik (Nature, 1936, 137, 741).—The val. obtained at 1·6° for D_2 is $32\cdot94\pm0\cdot04\times10^{-5}$ g.-cal. per cm. per sec. per degree. L. S. T.

Heat conductivity of liquid helium. W. H. Keesom and (Miss) A. P. Keesom (Physica, 1936, 3, 359—360).—The thermal conductivity of liquid He II at 1·4° and 1·75° abs. is about 190 g.-cal. per degree cm. sec., or 200 times that of Cu at room temp. and 3×10^6 that of liquid He I. The term "supra-heat conductivity" is suggested for this phenomenon. J. W. S.

Theory of viscosity of liquids. D. B. Macleod (Trans. Faraday Soc., 1936, 32, 872—876).—An equation of the type of Andrade (A., 1934, 356) can be deduced from the author's equation for η (A., 1925, ii, 498) by taking into account associative van der Waals forces. L. J. J.

Significance of viscosity. H. R. Schulz (Z. Physik, 1936, 99, 666—668).—Greases are colloidal solutions, and may be used to determine the dependence of the coeff. of viscosity on time, temp., and shearing forces. A. B. D. C.

Viscosities of some liquid refrigerants. J. H. Awbery and E. Griffiths (Proc. Physical Soc., 1936, 48, 372—380).—Using the method of timing the rate of fall of a closely fitting plug in a vertical tube filled with the liquid, and a special arrangement to prevent evaporation and bubble formation, data were obtained for η for SO_2, MeCl, EtCl, CCl_2F_2, *cis*- and *trans*-$C_2H_2Cl_2$, and $CHCl_3$, over the range −15° to 30°. Results follow the law $\eta=Ae^{a/T}$, where *T* is the abs. temp. and *A* and *a* are consts. N. M. B.

Structure viscosity. W. Philippoff (Z. Spiritusind., 1936, 59, 157—158).—A survey of apparatus and technique, and discussion of published date for starch. E. S. H.

Theory of structure viscosity. II. Streaming of structure-viscous substances. W. Philippoff (Kolloid-Z., 1936, 75, 142—154; cf. A., 1935, 692).—Published work is discussed. E. S. H.

Heterogeneous recombination and diffusion coefficients of halogen atoms. E. Rabinowitch and W. C. Wood (Trans. Faraday Soc., 1936, 32, 917—922).—The mechanism of heterogeneous recombination is discussed. Diffusion coeffs. of Br and I atoms through a no. of gases are calc. from measurements of the stationary dissociation of illuminated halogen vapours. L. J. J.

Origin of the term "solute." (Sir) W. J. Pope (Nature, 1936, 137, 782). L. S. T.

Thermal diffusion in deuterium mixtures. K. E. Grew and B. E. Atkins (Proc. Physical Soc., 1936, 48, 415—420).—Measurements of thermal diffusion effects in H_2–N_2 and D_2–N_2 mixtures over the temp. range −190° to 100° indicate that H_2 and D_2 have the same type of mol. field. He–N_2 mixtures were also examined. N. M. B.

Compressibility of aqueous solutions. E. Brander (Soc. Scient. Fenn. Comm. Phys.-Math., 1936, 9, 1—8).—A theoretical expression for the compressibility of aq. solutions is developed which gives vals. in close agreement with recorded experimental data and with those calc. from Tammann's formula (A., 1896, ii, 13). R. C. M.

Apparent volumes and apparent compressibilities of solutes in solution. III. Unsaturated and supersaturated solutions of calcium nitrate. A. F. Scott and G. L. Bridger (J. Physical Chem., 1936, 40, 461—470).—*d* and compressibility coeffs. have been determined for both unsaturated and supersaturated solutions of $Ca(NO_3)_2$ at 35°. There is no definite evidence of the existence of separate hydrates in solution. The influence of concn. on the apparent mol. vol. and compressibility is discussed. d^{35} for cryst. $Ca(NO_3)_2$ is 1·896, in good agreement with previous vals. M. S. B.

Viscosity and density of carbamide solutions. N. D. Litvinov and A. I. Melnikova (J. Appl. Chem. Russ., 1936, 9, 583—588).—The η of 15—75% solutions at 15—90° is given by $1/\eta=(2{\cdot}4-0{\cdot}2c)t+0{\cdot}067c-0{\cdot}01209c^2+50{\cdot}463$; over the same range $d=1{\cdot}0074-0{\cdot}00048t+0{\cdot}0028c$. R. T.

Optical properties of liquid mixtures of ketones and alcohols. T. Tomonari (Z. physikal. Chem., 1936, B, 32, 202—221; cf. A., 1933, 669, 1114).—The sp. refractivity, r_L, of ketone–alcohol mixtures falls below the mixture rule val. by an amount which diminishes with increasing chain length of either component. The changes in *n*, *d*, and r_L of the mixtures caused by small amounts of acid decrease in the same order, owing to increasing shielding of the OH and CO groups by alkyl groups; the changes increase with fall of temp. Acid has no effect on the state of $COMe_2$–H_2O mixtures, for here there is extensive complex formation in absence of acid. R. C.

Specific heats and related properties of the binary system methyl alcohol–toluene. L. S. Mason and E. R. Washburn (J. Physical Chem., 1936, 40, 481—491).—Sp. heats, heats of mixing, vol. contraction on mixing, and *n* have been determined for MeOH–PhMe mixtures at 25° and 35°. Heat capacities are > and *n* < required by the additivity rule. Mixing is always accompanied by heat absorption. The thermal effects are most pronounced in mixtures containing only a small proportion of MeOH, and it is suggested that they are due to dissociation of associated MeOH into simpler mol. aggregates. Changes of vol. and of *n* are attributed to combination of MeOH with PhMe. M. S. B.

Thermal conductivity of water–glycerol mixtures. S. Erk and A. Keller (Physikal. Z., 1936, 37, 353—358).—Results for 18 to 88% glycerol at 6—72° are recorded and expressed in terms of an empirical equation. A. J. M.

Properties of illuminated iodine solutions. II. Negative absorption effect in benzene and other solvents. E. Rabinowitch and W. C. Wood (Trans. Faraday Soc., 1936, 32, 816—823).—I solutions in C_6H_6, MeOH, and H_2O show during strong illumination a reversible increase in their extinction coeff. which is $\propto\sqrt{}$(light intensity) and independent of [I] (cf. this vol., 437). For solutions in CCl_4–C_6H_6 mixtures the effect is $\propto [C_6H_6]$. Explanations are suggested. F. L. U.

Mutually surface-active liquids. Mixtures of sulphuric acid with nitrobenzene and with ether. K. C. Bailey (J.C.S., 1936, 684—686).—Surface tension–composition curves for H_2SO_4–$PhNO_2$ and H_2SO_4–Et_2O mixtures both show a min. at a small % of H_2SO_4. F. L. U.

B.p. and composition of the vapour phase in the ternary system sulphuric acid–nitric acid–water. V. A. Kireev, I. J. Klinov, and A. N. Grigorovitsch (J. Chem. Ind. Russ., 1936, 13, 346—348). R. T.

Physical properties of the system ethyl alcohol–glycerol–water. R. C. Ernst, C. H. Watkins, and H. H. Ruwe (J. Physical. Chem., 1936, 40, 627—635).—Surface tensions, viscosities, *d*, *n*, and sp. heats have been determined at 25°. E. S. H.

Commercially important systems of organic solvents. Vapour–liquid equilibrium data for the ternary system *n*-butanol–*n*-butyl acetate–water. A. S. Brunjes and C. C. Furnas (Ind. Eng. Chem., 1936, 28, 573—580).—Equilibrium data at 25° are presented together with the *d* of ternary mixtures both saturated and unsaturated. It is shown that the composition of an unknown mixture of the alcohol and ester may be derived from a measurement of the amount of H_2O dissolved by the mixture. A saturated three-phase system when distilled leaves residues with a smaller H_2O content than the distillate, *i.e.*, there is no true ternary azeotropic mixture. The azeotrope of Bu^aOAc–H_2O has b.p. 95·5°/760 mm. and contains 29·44 mol.-% of BuOAc. J. L. D.

Vapour pressure of hydrogen fluoride, silicon fluoride, and water over solutions of the system HF–H_2SiF_6–H_2SO_4–H_2O. N. Chajdukov, Z. Linetzkaja, and A. Bognovarov (J. Appl. Chem. Russ., 1936, 9, 439—445).—V.-p. data are recorded for the systems HF–H_2O and HF–H_2SiF_6–H_2SO_4–H_2O at 25—75°. R. T.

Application of the quantum theory of metals to the phase equilibrium in alloys. S. T. Konobejevski (Ann. Physik, 1936, [v], 26, 97—115).—Theoretical. The Hume-Rothery phase types (A., 1928, 111) represent energy minima corresponding with definite electron-gas concns. The thermodynamics of equilibria involving solid solutions are discussed from this viewpoint. L. J. J.

Intermetallic compounds and mixed crystals. U. Dehlinger (Naturwiss., 1936, 24, 391—395).—A summary.

***X*-Ray investigation of the equilibrium diagrams of aluminium–lithium alloys and the structure of AlLi.** G. Komovski and A. Maximov (Z. Krist., 1936, 92, 275—283).—The equilibrium diagram up to 20·5% Li confirms the existence of two phases, α and β. The β-phase is a compound AlLi which is cubic, a_0 6·37 A., with 16 atoms in the unit cell. The character of the α-phase is not determined. B. W. R.

Thermal and electrical conductivities of metals and alloys. II. Heat-resistant alloys from 0° to 800°. R. W. Powell (Proc. Physical Soc., 1936, 48, 381—392; cf. A., 1934, 1282).—Thermal conductivities, obtained by a comparative longitudinal-flow method, and electrical resistivities and Lorenz functions have been determined for various special steels, monel metal, and a Ni (80%)–Cr (20%) alloy, for temp. up to 800°. The Lorenz functions are abnormally high at room temp., but decrease with rise of temp. to a common val. at 800° of about $0{\cdot}62\times10^{-8}$—$0{\cdot}68\times10^{-8}$. Results indicate that the thermal conductivity of a metal can be approx. predicted from the electrical resistivity with an accuracy which increases with rise of temp. N. M. B.

Electrical conductivity and phase diagram of binary alloys. The system sodium–lead. H. Klaiber (Z. Elektrochem., 1936, **42**, 258—264).—Conductivities have been obtained for alloys containing up to 40 at.-% Na at temp. from 50° to 300°. The decrease in κ with increase in [Na] is discontinuous. There is no evidence for the formation of Na_2Pb_5 as is suggested by the existence of a max. in the m.-p. curve. A phase diagram has been constructed. C. R. H.

Cobalt–molybdenum system. W. P. Sykes and H. F. Graff (Trans. Amer. Soc. Met., 1935, **23**, 249—283).—The solid solubility of Mo in Co decreases from 26% at the eutectic temp. (1300°) to $< 2\%$ at 700°. The eutectic contains the hexagonal Co-rich solid solution (γ), and ε, a phase of formula CoMo. ε is formed from the melt, on cooling, by a peritectic reaction at 1550° between the Co-rich liquid and the η-phase (Co_2Mo_3). The η-phase forms at 1020° on cooling from the melt by a second peritectic reaction between the Co-rich liquid and the Mo-rich δ-phase. η decomposes at 1250° on cooling into ε and δ. The δ-phase is the Mo-rich solid solution (3% Co at 1600°). The face-centered cubic form of Co extends to 25% of Mo at 1310°, at which temp. it forms as the β-phase on cooling the hexagonal solid solution ($\gamma+\varepsilon \rightleftharpoons \beta$). At 1200° a hexagonal phase (θ) forms by the reaction $\beta+\varepsilon \rightleftharpoons \theta$. θ is stable at 1200—1050°. The transformation point of Co at 1020° is raised to approx. 1310° by 25% of Mo. The lower point (420°) is depressed to 240° by 1—2% of Mo. The Co-rich solid solution, β, undergoes age-hardening at $> 450°$. Max. hardness is observed in an alloy of Co with 15% Mo when aged for 100 hr. at 550°. Ch. Abs. (*e*)

Properties of Heusler's alloy, and the true specific heat of manganese and its discontinuity. J. R. Ashworth (Proc. Physical Soc., 1936, **48**, 456—468).—Measurements of density, intensity of magnetisation, crit. temp., Curie const., electrical resistivity and its temp. coeff., thermoelectric power, and sp. heat are recorded. The true sp. heat of Mn shows a very marked discontinuity at about 350°, near the crit. temp. of Heusler's alloy. The heat capacity of the alloy is additive, both above and below the crit. temp.; this is also true for magnetite. N. M. B.

Problem of mixed crystals; Na–AgCl and Tl–CsCl mixed crystals with Al and Cr *X*-rays. H. O'Daniel (Z. Krist., 1936, **92**, 221—252; cf. this vol., 676).—The energy relations of superlattices in mixed crystals are discussed, and an attempt is made to locate these lattices in Na–AgCl and Tl–CsCl mixed crystals, using *X*-radiation both of normal and of rather long λ. B. W. R.

Permeability of palladium to hydrogen. Loss of diffusion power of pure palladium when heated. Regeneration of poisoned palladium. V. Lombard, C. Eichner, and M. Albert (Compt. rend., 1936, **202**, 1777—1779).—A disc of pure Pd suffers a progressive and irreversible loss of diffusive power on prolonged heating above 500—520° in presence of H_2, this loss being the more rapid the higher is the temp. This poisoning is arrested by lowering the temp. to < 450—500°. It thus appears that the state of max. permeability only is characteristic of the metal. The diffusive power can be restored considerably by heating to 500° in a current of air, cooling in air, and reducing the oxide film produced in H_2 at $< 140°$. The loss of diffusive power is probably due to agglomeration of the fine surface granules. J. W. S.

Temperature coefficient of solubility of hydrogen in organic solvents. E. B. Maxted and C. H. Moon (Trans. Faraday Soc., 1936, **32**, 769—775).—The solubility of H_2 in C_6H_6, $CHCl_3$, EtOH, AcOH, and EtOAc has been determined over a wide range of temp. between 0° and 75°. In each case the temp. coeff. is positive. F. L. U.

Solubility of carbon dioxide in aqueous solutions containing alcohol and sugars [at 15°]. H. A. Showalter and J. B. Ferguson (Canad. J. Res., 1936, **14**, 120—126).—The absorption coeff., α, decreases approx. linearly with increasing concn. of sucrose, glucose, and fructose. J. G. A. G.

Desorption of gases from aqueous solutions into air. I. G. Nagatkin (J. Appl. Chem. Russ., 1936, **9**, 434—438).—The rate of desaturation of aq. solutions of CO_2, H_2S, Cl_2, and O_2 when air is passed at const. velocity over the surface of the solution is $\propto$ the depth of the column of solution, to the mol. wt. and dipole moment of the solute, and to its degree of association. The experimental data are in agreement with Guyer's equation (A., 1934, 483). R. T.

Active oxides. XCIX. Solubilities of a mixture of magnesium and ferric oxides during the course of ageing. G. F. Hüttig and E. Zeidler (Kolloid-Z., 1936, **75**, 170—184; cf. this vol., 441).—The solubility in dil. HCl of ignited MgO or Fe_2O_3 is a more const. quantity the higher is the temp. of ignition. With equimol. mixtures the solubility and variation with age pass through max. and min. as the temp. of ignition is raised. E. S. H.

Solubility and activity coefficient of silver acetate in mixed solvents. F. H. MacDougall and C. E. Bartsch (J. Physical Chem., 1936, **40**, 649—659).—Solubilities of AgOAc at 25° in 10, 20, and 30% EtOH–H_2O in presence of K, Na, Li, Ca, Sr, and Ba nitrates have been determined. The solubility of AgOAc in H_2O at 25° is 0·06634 g.-mol. per litre. The Debye–Hückel equation is valid for the solutions investigated. Vals. of the mean ionic diameter are calc. for solutions containing KNO_3 or $NaNO_3$. The activity coeff. of AgOAc in saturated solutions in EtOH–H_2O mixtures without added nitrates has been calc. E. S. H.

Solubility of *d*-valine in water. J. B. Dalton and C. L. A. Schmidt (J. Gen. Physiol., 1936, **19**, 767—771).—The solubility between 0° and 60° varies with the cryst. form. H. G. R.

Solubilities of the dihalogenated *l*-tyrosines in ethyl alcohol–water mixtures. P. S. Winnek and

C. L. A. Schmidt (J. Gen. Physiol., 1935, **19**, 773—780).—The solubilities of dihalogenated *l*-tyrosines are first increased by the addition of EtOH and then decreased, whereas that of *l*-tyrosine is decreased. The apparent heat of dissolution of di-iodotyrosine in EtOH–H_2O and the solubility of *dl*-thyroxine at 30° in org. solvents have been determined. H. G. R.

Distribution of picric acid between benzene and mixtures of light and heavy water. P. Gross and A. Wischin (Trans. Faraday Soc., 1936, **32**, 879—883).—The distribution const. with pure D_2O at 18° is 4 times that with pure H_2O; it is not a linear function of the D_2O content. The effect is due to the different zero-point energies in the D and H linkings. L. J. J.

Structural changes taking place during the ageing of precipitates. X. Distribution coefficient of lead between the surface of barium sulphate and solution. Determination of specific surface of barium sulphate. I. M. Kolthoff and W. M. MacNevin (J. Amer. Chem. Soc., 1936, **58**, 725—728; cf. this vol., 561).—The distribution coeff., *K*, of $PbSO_4$ between $BaSO_4$ and H_2O is 0·12, and 0·067 between $BaSO_4$ and 50% EtOH at 25°. *K* decreases with increasing mol.-% of $PbSO_4$ in the surface of $BaSO_4$. The determination of the sp. surface of aged $BaSO_4$ ppts. by the radioactive method is described. E. S. H.

Anomalous distribution of thorium-C″ between uni- and ter-valent thallium ions. J. Zirkler (Z. Physik, 1936, **99**, 669—670).—Further evidence is given for the distribution previously recorded (cf. this vol., 282). A. B. D. C.

Sorption of sulphur dioxide by active charcoal. VII. Sorption equilibrium at low temperatures. K. Arii (Bull. Inst. Phys. Chem. Res. Japan, 1936, **15**, 254—265; cf. this vol., 153).—Sorption of SO_2 between −40° and −10° on charcoal activated at 800° may be represented by the isotherms of Patrick or Gregg. R. S.

Reversibility of adsorption of dissolved substances on ash-free charcoal. L. Lepin and G. Strachova (Z. physikal. Chem., 1936, **176**, 303—312).—For AcOH, the adsorption of which is essentially of the van der Waals type, the adsorption and desorption isotherms practically coincide. For HCO_2H, the adsorption of which is partly mol. and partly due to surface reaction of the CO_2H groups, the curves deviate somewhat, whilst with HCl and H_2SO_4, which are adsorbed mainly by surface reaction, the curves deviate widely. On readsorption after desorption the system moves back to the adsorption isotherm and vice versa. These observations are satisfactorily explained on the basis of Schilov's theory of surface compounds. R. C.

Mechanism of desorption of solvent vapours from active charcoal. I. A. P. Okatov and Z. I. Levina (J. Appl. Chem. Russ., 1936, **9**, 287—297).—Adsorbed EtOH is removed more easily than Et_2O from C by a current of steam. In general, the energy required for desorption $\propto$ the activity of the C, and the use of highly active C for solvent recovery is not therefore always advantageous. R. T.

Adsorption of the heavier rare gases by mercury. H. M. Cassel and K. Neugebauer (J. Physical Chem., 1936, **40**, 523—530).—The surface tension of Hg in contact with Kr at 235° and 253° abs. and with Xe at temp. between 237° and 293° abs. has been measured at various pressures. The adsorbed quantities have been calc. by Gibbs' equation. The heats of adsorption are also derived and compared with the theoretical vals. on the basis of the dispersion theory of the van der Waals forces. M. S. B.

Adsorption of gases by glass walls. XIV. Kinetics of the adsorption of carbon dioxide by Jena glass. V. Aleixandre (Anal. Fis. Quím., 1936, **34**, 315—319).—Using the technique employed previously (A., 1926, 1002), the adsorption of CO_2 by Jena glass between 760 and 190 mm. at 16° is found to be 0·25 of the adsorption by ordinary glass. The velocity of adsorption cannot be determined owing to the small quantities involved. F. R. G.

Sorption of gases by titania gel. II. Relation between the pressure and the sorbed amount of sulphur dioxide. I. Higuti (Bull. Inst. Phys. Chem. Res. Japan, 1936, **15**, 266—285; cf. A., 1935, 1315).—Sorption and desorption between −40° and 40° have been studied and the results are considered in relation to current theories. The hysteresis phenomena can be explained by the capillary adsorption theory. R. S.

Chemisorption of carbon dioxide by reduced iron. Influence of the chemisorption on van der Waals adsorption of carbon dioxide at 0°. K. Kawakita (Proc. Imp. Acad. Tokyo, 1936, **12**, 61—63).—The van der Waals adsorption (*a*) of CO_2, which occurs rapidly at 0°, has been studied with Fe on which CO_2 has been chemisorbed at 300—400° [when $Fe+CO_2$ (ads.)$=Fe_xO_y+CO$ (ads.) and 2CO (ads.)$=C+CO_2$ (ads.), the first reaction occurring only on active Fe centres and the second even on weak centres]. *a* is independent of the amount of chemisorption and time of evacuation after chemisorption, but is less if the desorption is performed at 0° than at 300—400°. With no evacuation after chemisorption *a* is small. The no. of adsorption centres for *a* on a fresh surface at 0° is approx. half that for a surface on which CO_2 has been chemisorbed at 300—400° and evacuated at the same temp., but the fraction of surface covered is approx. the same. R. S. B.

Activated adsorption of hydrogen on chromic oxide gel. Effect of gas pressure. R. L. Burwell, jun., and H. S. Taylor (J. Amer. Chem. Soc., 1936, **58**, 697—705).—Rates of adsorption have been measured at 195—491° abs. and 0·125—1 atm. The data show that the surface of Cr_2O_3 gel is composite, with areas of characteristic activation energies ranging from low vals. to 21·7 kg.-cal. per mol. for a large and relatively uniform area. The influence of temp., pressure, and occupied surface on the velocity of adsorption on such an area has been examined. The slow process of adsorption appears to be an interaction between mols. adsorbed by van der Waals forces and surface atoms which receive the necessary surface energy. E. S. H.

Sorption of water vapour from air by means of silica gel. E. L. Kopelovitsch and N. I. Troitzkaja (J. Appl. Chem. Russ., 1936, **9**, 673—680).—Max. sorption is shown by acid-treated SiO_2 gel which is characterised by its high percentage of small pores, and by the high apparent *d* (0·65) of the dry powder. Sorption of H_2O is favoured by low temp. and high partial H_2O pressure. H_2O is removed from saturated gel at 200° (75—90 min.). R. T.

Ionic exchange and sorption of gases by chabasite. E. Rabinowitch and W. C. Wood (Trans. Faraday Soc., 1936, **32**, 947—956; cf. A., 1932, 458).—The sorption of H_2 (at $-190°$), N_2 ($-190°$ and $-80°$), CO_2 (20°), and C_3H_6 (20°) by a no. of chabasites (I) in which the Ca was replaced by a series of different cations, have been measured. Ca-, Sr-, and Ba-(I) have approx. identical sorption properties. With Cd-(I), sorption is less at low pressure, but the saturation val. is the same. The sorption capacity is abnormally low for N_2 and C_3H_6 on Na-(I), and for N_2, H_2, and C_3H_6 on K-(I). The results are discussed. L. J. J.

Adsorption of electrolytes on crystal surfaces. I. M. Kolthoff (Chem. Weekblad, 1936, **33**, 321—324).—Polemical against de Brouckère (this vol., 422). D. R. D.

Effect of irradiation on adsorptive power of solids. I. J. A. Hedvall [with E. Fridén, T. Lindstrand, and E. Svenander] (Z. physikal. Chem., 1936, **B**, **32**, 383—395).—The previously reported increase in adsorptive power, *A*, of phosphors during illumination (A., 1935, 1055) has been confirmed by further experiments. Ultra-violet light causes a greater increase than does white light. When irradiation ceases, *A* declines progressively, but tends to constancy at a val. $\geqslant$ is observed when there has been no irradiation. Substances other than phosphors exhibit similar effects on appropriate irradiation. Attempts to detect differences in the rate of dissolution of fluorophors in the light and in the dark have yielded negative results. R. C.

Determination of heats of sorption from solutions at crystal surfaces. N. A. Held and I. A. Khainsky (Kolloid-Z., 1936, **75**, 287—288).—Preliminary results for the adsorption of Na oleate in aq. solution by $BaSO_4$ are reported. E. S. H.

Adsorption of proteins. Influence of salts on the adsorption of hæmoglobin by kaolin. M. Paić and (Mlle.) V. Deutsch (Compt. rend., 1936, **202**, 1514—1516; cf. this vol., 676).—The adsorption is diminished by 0·1—1N-$Na^{\cdot}$, -$K^{\cdot}$, and -$Ba^{\cdot\cdot}$ and by N-SO_4''. The diminution produced by NaCNS and Na_3PO_4 is mainly due to the increase in p_H. R. S.

Adsorption of nitrogenous substances from aqueous solutions.—See this vol., 914.

Binding of glacial phosphoric acid by the proteins of wheat flour. L. W. Samuel and R. K. Schofield (Trans. Faraday Soc., 1936, **32**, 760—769; cf. A., 1935, 300).—The capacity of 37 wheat flours to bind glacial phosphoric acid has been found by electrometric titration to vary from 6·7 to 10·1 milliequiv. per 100 g. of flour. Flours of higher N content tend to bind more acid per g. of flour but less per g. of protein. The uptake per g. of gluten varies only slightly with acid concn. between 0·02 and 1·0N. Flour proteins do not bind the various (HPO_3) units in the proportion in which they exist in the original acid solution. F. L. U.

Reduction of some adsorbed oxidation–reduction indicators. H. A. Abramson and I. R. Taylor (J. Physiol. Chem., 1936, **40**, 519—521).—Experiments on the reduction and re-oxidation of methylene-blue, litmus, and phenosafranine adsorbed on filter-paper indicate that the bonds responsible for adsorption do not affect appreciably those groups which are involved in the oxidation–reduction process. The ionisation of adsorbed protein is a similar example of this type of behaviour. A surface which adsorbs selectively one of the constituents of a reversible oxidation–reduction system may thus alter the oxidation–reduction potential. Data for p_H indicators are discussed in this connexion. M. S. B.

Polarisation of the luminescence of dyes adsorbed on colloidal gels. P. Pringsheim and H. Vogels (J. Chim. phys., 1936, **33**, 261—271).—The rate and character of the fixation of dyes on SiO_2 gel have been studied by measuring the degree of polarisation (*p*) of the fluorescence. The *p*–time curves have the general form of adsorption curves. The amount of adsorption varies considerably with the solvent. The fluorescence appears to be due to adsorbed ions and not to mols. M. S. B.

Absorption and accumulation of solutes by living plant cells.—See this vol., 907.

Simple kinetic theory of ionic exchange. I. Ions of equal valency. H. Jenny (J. Physical Chem., 1936, **40**, 501—517).—A model for the mechanism of ionic exchange is described and an exchange adsorption isotherm derived which is verified by ionic exchange data for Putnam clay. The structure of the colloidal particles is apparently important. The equation is satisfactory for soil colloids and bentonite clays, all of which have plate-like structures and seem to exchange on the outer surface only; it is less satisfactory for permutites and certain zeolites which have ultra-microscopic pores and channels. If there are large differences in the nature of the exchanging ions discrepancies may also occur. There is a relationship between the base-exchange const. and the ratio of the electric potentials of the double layers, which suggests that ionic exchange is connected with the question of colloid stability. M. S. B.

Theory of formation of surface films on metals. II. C. Wagner (Z. physikal. Chem., 1936, **B**, **32**, 447—462).—The theory previously advanced (A., 1933, 564) has been combined with the results of the misplacement theory of electrical conductivity (*ibid.*, 888) to obtain relations between the rate of formation of surface films, *k*, and the pressure of the reacting gas, *p*. The diffusion coeffs. for the equalisation of concns. in ionic lattices deviating in composition from the integral stoicheiometric ratio have been calc. for various types of misplacement. For film formation on Ag by Cl_2 and Br_2 the parabolic

law (A., 1922, ii, 831) is valid and, as the above theory requires, $k \propto \sqrt{p}$. From the observed vals. of k it is calc. that for AgBr at 200° and $p=0{\cdot}23$ atm. the electrons are responsible for 17% of the conductivity; the observed val. is 12%. It is inferred that diffusion during film formation consists in the migration of equiv. amounts of $Ag^{\cdot}$ ions and electrons from the metal through the film to the outer surface, where the real chemical reaction occurs. The conductivity is thus of the electron deficiency type.
R. C.

Composition and structure of surface films on iron. E. A. Nikiforov and N. A. Godina (J. Appl. Chem. Russ., 1936, 9, 225—228). R. T.

Mobility of potassium on tungsten. R. C. L. Bosworth (Proc. Roy. Soc., 1936, **A**, **154**, 112—123).—The diffusion coeff. for the surface migration of films of K on W rises with increasing concn., whilst the associated activation energy falls. The activation energy of diffusion for an infinitely dil. film=0·72 volt, and for a unimol. film=0·29 volt. This fall in the val. is due to the existence of a spreading force caused by the mutual repulsion of the adions. The effective dipole moment of the adions has been calc. from vals. of the spreading force at different surface concns. L. L. B.

Diffusion of gases from capillary tubes. G. Costeanu and P. Renaud (Compt. rend., 1936, **202**, 1511—1514).—When a stream of H_2O vapour at low pressure from a capillary tube impinges on Na, or a current of air containing H_2S strikes a gelatin surface containing $Pb(OAc)_2$, concentric annular stains are produced. R. S.

Mechanism of the rise of hydrosols and coloured solutions through porous materials. A. Boutaric and (Mlle.) P. Berther (Compt. rend., 1936, **202**, 1781—1783; cf. A., 1934, 840).—The fact that rise of sol particles or coloured ions through porous material (*e.g.*, filter-paper) does not cease when the solute reaches the top of the porous material is explained by solute continuing to rise, owing to evaporation and to progressive swelling of the porous material. J. W. S.

Determination of Zsigmondy's gold number, foam number, and surface tension of sodium and potassium salts of saturated and unsaturated fatty acids. N. N. Godbole and M. Sadgopal (Kolloid-Z., 1936, **75**, 193—201).—Data for K and Na salts of saturated fatty acids (C_4—C_{18}) and for unsaturated and hydroxy-C_{18} acids are recorded and discussed from the viewpoint of detergent requirements. E. S. H.

Energy transformations at interfaces. H. Kautsky (Kolloid-Z., 1936, **75**, 164—169).—The adsorption of the three tautomeric aminophthalic acid hydrazides by basic and acid gels has been studied. The absorbates show different colours of fluorescence, corresponding with the several tautomerides which are obtained under different conditions of prep.
E. S. H.

Creeping of saturated salt solutions. T. H. Hazlehurst, jun., H. C. Martin, and L. Brewer (J. Physical Chem., 1936, **40**, 439—452; cf. Washburn, A., 1927, 931).—Creeping of a solution over a surface is attributed to the preferential wetting of the surface by the solid solute. Previous views of the mechanism are considered and the influence of the nature of the supporting surface, the crystal habit of the solute, and the free surface energies involved are discussed. M. S. B.

Osmotic complexes in which the pressure can differ on the two sides of the membrane. F. A. H. Schreinemakers and J. P. Werre (Rec. trav. chim., 1936, **55**, 301—314).—Pressure and vol. changes which take place during osmosis in complex systems characterised by various combinations of liquids are considered. C. R. H.

Action of allylamine and Novalgin on prepared animal membranes (goldbeater's skins). R. Raff and E. Abrahamczik (Z. ges. exp. Med., 1935, **95**, 691—702; Chem. Zentr., 1935, ii, 1562).—Allylamine (I) and allyl formate increase the permeability to H_2O; treatment with Novalgin checks the deterioration caused by (I). H. N. R.

Preparation of isotonic solutions. H. Böhme (Arch. Pharm., 1936, **274**, 255—267). R. S. C.

F.p. of aqueous solutions. X. Dioxan and its mixtures with lithium, sodium, and potassium chlorides. G. Scatchard and M. A. Benedict (J. Amer. Chem. Soc., 1936, **58**, 837—842; cf. A., 1935, 30).—The f.p. of aq. dioxan containing KCl, NaCl, or LiCl up to a total concn. of dioxan+ions of $2M$ have been determined. At low concns. the osmotic coeffs. of the mixtures are < the Debye–McAulay theory requires, but agree well with the second theory of Debye. The salting-out effects of M-salt solutions calc. from these results have nearly the same relative vals. as those measured directly for Et_2O. E. S. H.

Dielectric constants of solutions of organic acids in ethyl alcohol and benzene. R. C. Gore and H. T. Briscoe (J. Physical Chem., 1936, **40**, 619—625).—Solutions of 24 org. acids at concns. up to 100 mg.-mol. per litre have been examined. The curves are compared with those relating n and resistance functions of the same solutions with concn. The results show that the electrical saturation theory holds qualitatively in some cases, but not quantitatively. EtOH has dielectric const. 24·33 at 25° and n_D^{25} 1·35921. E. S. H.

Mechanism of quenching of fluorescence in solutions. J. Weiss and H. Fischgold (Z. physikal. Chem., 1936, **B**, **32**, 135—138).—The quenching may be regarded as a simple electron transfer from the quenching ion to the excited mol., Fl*, *e.g.*, $Fl^*+Fe^{\cdot\cdot} \rightarrow Fl'+Fe^{\cdot\cdot\cdot}$, or, in a heterogeneous system on a metal surface, $Fl^*+Pt \rightarrow Fl'+Pt^{\cdot}$. The energy of excitation of Fl has the effect of increased electro-affinity. In the homogeneous reaction with $Fe^{\cdot\cdot}$ at higher light intensities in absence of O_2 practically irreversible reduction may occur or a reversible photostationary state be set up, depending on the conditions. R. C.

Significance of van der Waals forces for properties of salt solutions. G. Kortüm (Z. Elektrochem., 1936, **42**, 287—292; cf. this vol., 425).—The importance of van der Waals forces between ions and solvent mols. is discussed. F. L. U.

Velocity of fall of "super-Stokes" particles. N. Fuchs (Tech. Phys. U.S.S.R., 1936, **3**, 254—257).—Theoretical. The validity of Stokes' law for small spheres has been studied. Calculations for solid particles of *d* 4—12 falling in air show that Stokes' law ceases to apply at radius 10 μ. Fluid particles, which flatten on falling, will have a smaller velocity than the calc. val. R. S. B.

Preparation of gold sol. A. C. Honig (Pharm. Weekblad, 1936, **73**, 614—617).—Au sols made from H_2O twice distilled in glass are not transparent. Transparency depends on the presence of traces of Sn in the solution and consistently good sols are obtained by using such H_2O collected in glass vessels containing a Sn rod. In the method recommended, 2·5 c.c. of 1% $AuCl_3$, 2·63 c.c. of 0·2N-K_2CO_3, and 0·125 c.c. of 1% $H_2C_2O_4$ solutions are added to 250 c.c. of the boiling H_2O, the flask is removed from the flame, and 3 c.c. of 1% CH_2O solution are added with shaking. S. C.

Negative ferric hydroxide sol. Preparation. A. Das and R. De (J. Indian Chem. Soc., 1936, **13**, 197—203).—Neutral $Fe(OH)_3$ sol can be prepared by mixing equimol. quantities of $FeCl_3$ and NaOH solutions in the presence of a stabiliser, *e.g.*, alkaline citrate, tartrate, phosphate, silicate, sulphide, or carbonate, the stabilising effect decreasing in this order. C. R. H.

Organosol of sulphur. K. Inaba (Bull. Inst. Phys. Chem. Res. Japan, 1936, **15**, 298—300).—Amorphous S is pptd. from $Na_2S_2O_3$ by HCl, dissolved in C_6H_6 or EtOH, and the organosol obtained by irradiation with ultra-violet light. A no. of sols have been prepared for clinical use by distillation of C_6H_6 from a mixture of "benzosol" and fat or oil. R. S.

Synthesis of hydrosols of sparingly-soluble salts by electrolysis. II. Ferric phosphate hydrosols. B. G. Saprometov and E. I. Smoligina (Kolloid-Z., 1936, **75**, 291—297; cf. A., 1934, 1305).—The optimal conditions (c.d., temp., and concn. of Na_2HPO_4) for the prep. of $FePO_4$ sols have been determined. For the more stable sols the dispersity, ζ potential, and resistance to flocculation by KCl have been determined. E. S. H.

Liquid ammonia as a solvent. V. Metallic solutions. J. F. Chittum and H. Hunt (J. Physical Chem., 1936, **40**, 581—589).—Solutions of NH_4 in liquid NH_3 have been prepared by electrolysis of NH_4Cl at $-60°$ to $-80°$. Solutions of alkali metals in liquid NH_3 show the Tyndall effect; on electrodialysis the alkali metal does not pass through the membrane. Such systems are discussed as colloid solutions. E. S. H.

Physical chemistry of the autoclave process of sulphur melts. Formation and destruction of the three-phase sulphur emulsion. K. N. Samochvalov and O. S. Koshuchova (Kolloid-Z., 1936, **75**, 217—222).—The degree of emulsification in the system molten S–conc. aq. $MgCl_2$ and the type of emulsion (S as the inner or outer phase) have been studied under different conditions, using $CaSO_4$ or SiO_2 as emulsifiers. E. S. H.

Brownian movement of a linear lattice. I. Bessenov (Compt. rend. Acad. Sci. U.R.S.S., 1936, **1**, 323—327).—Mathematical. A. J. M.

Photographic observation of aërosol particles as an objective method of measurement. A. Winkel and W. Witt (Z. Elektrochem., 1936, **42**, 281—285).—An optically defined vol. of aërosol, illuminated from opposite directions by two high-power lamp systems on the same optical axis, is photomicrographed with an exposure of 0·1 sec. Very fine particles can be thus recorded, and photophoresis is prevented. In studying coagulation the photographic method is preferred to visual counting, owing to the elimination of personal errors, and to the possibility of photographing an aërosol within a few sec. of its formation, and thus obtaining points at an early stage in the coagulation process. Examples are given of the photographic study of Brownian movement, sedimentation under gravity, and electric mobility. F. L. U.

Behaviour of aërosols in the acoustic field. I. O. Brandt and E. Hiedemann (Kolloid-Z., 1936, **75**, 129—135).—Kinemato-micrographic investigation has shown that aërosols (smoke, NH_4Cl, etc.) are coagulated when subjected to sound or ultrasonic waves. The increase in particle size has been determined by measurements of light absorption and rate of fall. E. S. H.

Determination of size of micelles from the swelling of films. S. Papkov (J. Appl. Chem. Russ., 1936, **9**, 518—519).—Polemical, against Voskresenski (B., 1935, 719). R. T.

Colour and opacity of emulsions. J. F. Morse (Trans. Faraday Soc., 1936, **32**, 941—947).—A photoelectric photo-colorimeter is described. In a coloured emulsion the tone increases with degree of dispersion. Data are recorded for opacities of paraffin–aq. gum solution emulsions at different concns. and degrees of dispersion. For emulsions of grain size 1 μ, the opacity is independent of concn. for concns. $> 5\%$. L. J. J.

Dielectric constant of colloidal systems. J. T. G. Overbeek (Natuurwetensch. Tijds., 1936, **18**, 55—72).—The ε of colloidal systems with H_2O as the disperse medium is affected by (1) differences in ε of the disperse phase and disperse medium, which may increase or decrease ε; (2) the electric double layer effect, as yet unconfirmed experimentally, which will increase ε; (3) the permanent dipole moment of the particles increasing ε at low ν, confirmed with lyophilic colloids; (4) hydration decreasing ε at high ν but increasing ε at low ν. This last has been confirmed experimentally but an adequate explanation of the phenomenon is wanting. S. C.

Diffusion potentials in colloidal systems. H. B. Steinbach (J. Cell. Comp. Physiol., 1935, **7**, 291—300).—The potential between alkaline gelatin gels and applied electrolytes is considerable, and may be considered to be a diffusion potential between two electrolyte phases, the gel functioning as a slow-moving anion. R. N. C.

Double layer in colloids. H. R. KRUYT (Natuurwetensch. Tijds., 1936, 18, 29—37).—A lecture on the theory of the electric double layer in colloids. S. C.

Character of hydrophilic colloids. Hydration. H. R. KRUYT (Natuurwetensch. Tijds., 1936, 18, 38—43).—A lecture, discussing mainly dipole orientation in the hydration of colloids. S. C.

Colloid behaviour of polymeric carbohydrates : starch, cellulose, and glycogen. P. KOETS (Natuurwetensch. Tijds., 1936, 18, 44—54).—A lecture dealing principally with the internal hydration and the electrical states of these systems. S. C.

Mixtures of colloidal electrolytes with uni-univalent salts. J. W. MCBAIN and (MISS) J. SEARLES (J. Physical Chem., 1936, **40**, 463—499).—The electrical conductivity and f.-p. lowering of mixtures of ordinary electrolytes with alkali or H soaps are in good agreement with the additive mixture rule. The charges on the micelle are so widely spaced as to be practically independent. Thus the ionic strength of colloidal electrolytes is similar to that of uni-univalent electrolytes.
M. S. B.

Validity of the Lambert–Beer law in hydrophobic colloids. F. B. GRIBNAU, H. R. KRUYT, and L. S. ORNSTEIN (Kolloid-Z., 1936, **75**, 262—268).—Experiments with Au and Se hydrosols confirm the validity of the law. E. S. H.

Osmotic pressure of glycogen solutions.—See this vol., 878.

Viscosity and adsorption of starch sols. J. H. C. MERCKEL (Kolloid-Z., 1936, **75**, 318—322).—The influence of Na salts of monobasic acids on the η of starch sols and the adsorption of the same salts by starch are in accordance with the lyotropic series.
E. S. H.

Structure mechanics of viscous–elastic continua. I. Hydrodynamic theory of anomalous turbulence. H. UMSTÄTTER (Kolloid-Z., 1936, **75**, 135—142).—Mathematical. E. S. H.

Coagulation of colloids. XI. Variation of optical refractivity during the coagulation of colloidal manganese dioxide and new evidence for the discontinuity of the change. S. S. JOSHI and S. J. RAO (J. Indian Chem. Soc., 1936, **13**, 141—149).—Coagulation of colloidal MnO_2 by conc. solutions of inorg. salts has been followed by the measurement of *n*. Further evidence is obtained that coagulation proceeds through discontinuous stages termed " zones of coagulation." (Cf. this vol., 426.)
C. R. H.

Flocculation of stannic oxide sols. H. S. VAN KLOOSTER and A. PETROVICH (J. Physical Chem., 1936, **40**, 591—597).—The ease of peptisation of SnO_2 sols by alkalis is in the order KOH>NaOH>NH_4OH>LiOH. When the sols are treated with alkali-metal salts, the flocculation vals. of the cations are in the order K>Na>NH_4>Li, which indicates that colloidal SnO_2 has hydrophilic properties. Addition of alcohol lowers the amount of electrolyte required for coagulation. The significance of hydration of the flocculating ions is discussed.
E. S. H.

Electrolyte coagulation of weakly solvated sols and electrolyte activity. III. Flocculation by reversing electrolytes. WO. OSTWALD (Kolloid-Z., 1936, **75**, 297—317; cf. this vol., 157).—A crit. discussion of published work. E. S. H.

Liesegang rings of manganese sulphide. II. O. F. TOWER (J. Physical Chem., 1936, **40**, 599—602; cf. A., 1931, 924).—Periodic structures of MnS in SiO_2 gel were found to be spaced in geometrical progression. The influence of diffusion, supersaturation, and adsorption is discussed. E. S. H.

Quantitative analyses of Liesegang rings. A. T. LINCOLN and J. C. HILLYER (J. Physical Chem., 1936, **40**, 645—647).—Quant. analyses of periodic structures of $CuCrO_4$ in SiO_2 gel have been made. Comparison with the conditions of pptn. in absence of the gel shows that the SiO_2 gel inhibits the pptn. of $CuCrO_4$ until higher concns. are reached.
E. S. H.

Mixed crystal formation of zinc sulphide post-precipitated with mercuric sulphide. Ageing of mercuric sulphide and of zinc sulphide. R. MOLTZAU and I. M. KOLTHOFF (J. Physical Chem., 1936, **40**, 637—643).—*X*-Ray evidence shows that the ppts. form mixed crystals containing $\ngtr$ 12 mol.-% of ZnS. Ageing of the ppts. in the supernatant liquid at room temp. tends to perfect the cryst. state. Some of the variables affecting the transformation of black HgS to the red form have been noted.
E. S. H.

Effect of surface tension and electrical potential on the stability of mercury emulsions. V. SIVERTZ, W. H. NAYLOR, and H. V. TARTAR (J. Amer. Chem. Soc., 1936, **58**, 782—786).—The Hg–H_2O interfacial tension is raised by adding K citrate, tartrate, or chloride. There is no relation between change of interfacial tension or p_H of solution and ease of emulsification in this system. Electrocapillary curves show that emulsifying and non-emulsifying agents give similar results. E. S. H.

Dynamical principle of thixotropic solidification and its application. W. HELLER (Compt. rend., 1936, **202**, 1507—1509).—Thixotropy is defined and the conditions for its appearance in hydrophilic colloids are indicated. R. S.

Alumina gel, its preparation and properties. H. BRÜCKNER and L. HIRTH (Angew. Chem., 1936, **49**, 360—362).—When Al salt solutions, containing about 2% of $Al^{\cdots}$, are pptd. by adding 25% excess of aq. NH_3 and the product is washed repeatedly by decantation, an amorphous Al_2O_3 gel is obtained, which resembles SiO_2 gel. The relative rates of adsorption of H_2O vapour by amorphous and cryst. Al_2O_3 gel and SiO_2 gel have been compared. The amorphous Al_2O_3 gel takes up a *max.* of 40% H_2O and can be regenerated by heating in air at 400—500°.
E. S. H.

Hydroxide and oxyhydrate gels, and their amphoteric properties. A. KRAUSE (Kolloid-Z., 1936, **75**, 288—291).—Polemical (cf. this vol., 158).
E. S. H.

Gel system : cellulose nitrate–copper–bronze. W. E. GLOOR and H. M. SPURLIN (J. Amer. Chem. Soc., 1936, 58, 854—855).—Gelation in this system appears to be caused by a reaction between Cu in some form and NO_3' in the cellulose ester. The greater is the length of the chain mols. or the greater their concn., the less is the amount of bronzing powder required to form a stiff gel. E. S. H.

Determination of temperature of maximum density of gels. H. E. von Gronow (Z. anorg. Chem., 1936, **227**, 221—224).—The temp. of max. *d* of gelatin gels, calc. from the contraction occurring when gelatin is dissolved in H_2O, and from the respective coeffs. of expansion, agree with those observed by Taffel (J.C.S., 1922, **121**, 1971). The gels behave, on thermal expansion, precisely as if the gelatin were present in the form of anhyd. solid. F. L. U.

Bound water in gelatin gel. E. Hatschek (Trans. Faraday Soc., 1936, **32**, 787—789).—A direct demonstration of "bound" H_2O in gelatin gel is based on the colour change accompanying the dehydration of $CoCl_2,6H_2O$ contained in the gel. The change is complete when the H_2O content of the gel falls to 30·4—34·0%. F. L. U.

Gelation of different kinds of gelatin. R. Reiger and S. Bach (Kolloid-Z., 1936, **75**, 322—325).—Investigation of the change of optical rotation of gelatin during the initial stages of gelation shows that for 4 different kinds of gelatin the abs. change is different, but the relative change is the same. E. S. H.

Influence of ultrasonic waves on gels. H. Freundlich and K. Söllner (Trans. Faraday Soc., 1936, **32**, 966—970).—The liquefaction of thixotropic gels by ultrasonic waves is due to cavitation, and does not occur if this is prevented. L. J. J.

Physico-chemical properties of electrodialysed gels of silica, alumina, ferric hydroxide, and their mixture. I. Ion exchange. P. B. Bhattacharyya and K. Ganguli (J. Indian Chem. Soc., 1936, **13**, 204—213).—Dried electrodialysed gels of SiO_2, Fe_2O_3, Al_2O_3, and mixtures of SiO_2 and Fe_2O_3 or Al_2O_3 were treated with aq. solutions of NaCl, KCl, $CaCl_2$, and $MgCl_2$ and the amount of ion adsorption was measured. SiO_2 did not adsorb Cl′ ions. Cation adsorption in the case of the mixed gels was always > that calc. from the adsorption of the components. C. R. H.

Viscosity of thorium phosphate gel-forming mixtures during gelation. S. M. Mehta, M. U. Parmar, and M. Prasad (J. Indian Chem. Soc., 1936, **13**, 128—135).—The η of $Th_3(PO_4)_4$ during gelation, alone and in presence of $Th(NO_3)_4$ and H_3PO_4, has been investigated. The η increases with time, at first slowly and then more rapidly, but there is no evidence of discontinuity in the η–time curves during gelation. Additions of H_3PO_4 and $Th(NO_3)_4$ respectively increase and decrease the rate of increase of η with time, the former being due to an increase in the no. of micelles in unit vol., and the latter to Th ions peptising $Th_3(PO_4)_4$, and so increasing the degree of dispersion of the micelles. Non-electrolytes decrease and electrolytes increase the rate of increase of η with time. C. R. H.

Viscosity of fibrinogen.—See this vol., 874.

Isoelectric point of glycinin. R. J. Hartman and L. T. Cheng (J. Physical Chem., 1936, **40**, 453—459).—The electrophoresis of glycinin indicates that the isoelectric point is at p_H 5·02. Min. η, min. solubility, and min. variation of electrical conductivity with change of p_H are at the same point within the limits of experimental error. This result confirms Loeb's view that the physical properties of a protein are related to the isoelectric point. M. S. B.

Influence of mono- and poly-hydric alcohols and mono- and poly-saccharides on the absorption of fluid by gels. L. I. Weber and F. Lederer (Biochem. Z., 1936, **285**, 115—122).—A layer of H_2O or aq. solution of various non-electrolytes is placed above a gelatin gel and the effect on swelling noted. The power to remove H_2O from the gel increases with increasing no. of OH groups and with increasing mol. wt. Thus the effect increases in the series MeOH, EtOH, PrOH, $(CH_2{\cdot}OH)_2$, trimethylene glycol, β-butylene glycol and similarly in the series glycol, glycerol, erythritol, mannitol, glucose, maltose, sucrose, and lactose. Dextrin and starch have about the same action. The solubility of the solute has some effect but does not solely determine the degree of swelling. P. W. C.

Cataphoretic migration velocity of inorganic colloids. J. N. Mukherjee, S. G. Chaudhury, and B. N. Ghosh (Kolloid-Beih., 1936, **43**, 417—466).—A summary of published work. The influence of dilution, electrolytes, non-electrolytes, and their mixtures, and the relation of electrophoresis to dielectric const. and crit. coagulation potential are discussed. E. S. H.

Experimental test of the identity of electrokinetic potentials. Electrosmosis and streaming potential measurements with a glass slit. R. DuBois and A. H. Roberts (J. Physical Chem., 1936, **40**, 543—560).—ζ-potentials for very dil. aq. electrolytes (10^{-3}—$10^{-6}N$) obtained from electrosmosis experiments are nearly identical with those afforded by streaming potential measurements over most of the concn. range. Large discrepancies, however, occur at very low ionic concn. With $10^{-5}N$-$AlCl_3$ results of opposite sign are obtained by the two methods. M. S. B.

Exchange reactions between heavy water and hydrogen compounds.—See this vol., 819.

Effect of isotopy on the position of chemical equilibrium. J. M. Bijvoet (Chem. Weekblad, 1936, **33**, 287—288).—Isotopy has no effect on chemical equilibrium as far as statistical wt. is concerned. The explanation given by Giauque and Overstreet (A., 1932, 695) is criticised and a more rational one offered. S. C.

Equilibrium between ethyl alcohol, water, and ethyl ether in the gaseous phase. G. Semerano (Gazzetta, 1936, **66**, 162—169).—The equilibrium has been studied at 249° and 266° and 10—70 atm., using a mixture of Al oxide and phosphate as catalyst. From the linear relation between log *K* and *p*, the calc. vals. of K at 1 atm. are 7·25 and 7·69 at 249° and 266°, respectively. O. J. W.

Equilibrium between *n*-propyl alcohol, water, and *n*-propyl ether in the gaseous phase. G. SEMERANO (Gazzetta, 1936, **66**, 170—172; cf. preceding abstract).—From measurements up to 32 atm. between 235° and 260° the val. of K at 1 atm. and 250° is calc. to be 11·0. O. J. W.

Equilibrium between *n*-butyl alcohol, water, and *n*-butyl ether in the vapour state. G. SEMERANO (Gazzetta, 1936, **66**, 172—174; cf. preceding abstracts).—From measurements up to 20 atm. between 250° and 260° the calc. val. of K at 1 atm. and 250° is 14·0. O. J. W.

Cryoscopic determination of the total hydration of potassium iodide ions. (MLLE.) O. HUN (Compt. rend., 1936, **202**, 1779—1781).—The apparent cryoscopic const. (A., 1933, 460) for 0·5N-KI is 19·99, suggesting hydration represented by $KI,8{\cdot}6H_2O$ (cf. *ibid.*, 566; A., 1934, 728). J. W. S.

Dissociation constant of hydrochloric acid. R. A. ROBINSON (Trans. Faraday Soc., 1936, **32**, 743—744).—The const. $K=a_Ha_{Cl}/[\text{mol. fraction HCl}]$ (a=activity) has been derived for 0·56—15·4N-HCl from v.-p. data, assuming the validity of Raoult's law. K varies from 20×10^{-6} at 0° to $0{\cdot}12\times10^{-6}$ at 50°. Log K gives a linear plot with $1/T$, from which the heat of dissociation is calc. to be 17·9 kg.-cal. F. L. U.

Thermodynamics of hydrochloric acid in methyl alcohol–water mixtures from electromotive force measurements. H. S. HARNED and H. C. THOMAS (J. Amer. Chem. Soc., 1936, **58**, 761—766).—E.m.f. of the cells $H_2|HCl(m)$ in x% MeOH, y% $H_2O|AgCl$–Ag have been determined at 5° intervals from 0° to 40° in 10—20 wt.-% MeOH, with acid concns. of 0·003—2M. The activity coeff. of the acid in MeOH–H_2O mixtures of high dielectric const. can be calc. on the basis of the extended Debye–Hückel theory from the data for aq. solution. Methods of extrapolation of the e.m.f. data for the above cell have been studied and the standard potential of the cell in MeOH has been recalc. The e.m.f. of transfer of the acid at unit activity from one solvent to another is discussed in relation to the Born theory, and vals. for the sum of the reciprocals of the ionic radii have been obtained. Equations and parameters for calculating the relative partial mol. heat content and sp. heat of the acid in 10 and 20% MeOH solutions are given. E. S. H.

Second dissociation constant of carbonic acid. Y. KAUKO and V. MANTERE (Z. physikal. Chem., 1936, **176**, 187—201; cf. this vol., 29).—From the e.m.f. of the cell $H_2|Na_2CO_3|$saturated $KCl|0{\cdot}01N\text{-}HCl+0{\cdot}09N\text{-}KCl|H_2$ the $H^{\cdot}$ ion activity of $10^{-4}-10^{-3}M$-Na_2CO_3 has been determined, leading to vals. of the above dissociation const. at 0—37°, having a possible error of ±7%. The heat effect for the second dissociation is −2700 and −7500 kg.-cal. at 12·5—37° and 0—12·5°, respectively. R. C.

Chemical constitution and dissociation constants of monocarboxylic acids. V. Further substituted benzoic and phenylacetic acids. J. F. J. DIPPY and R. H. LEWIS (J.C.S., 1936, 644—649; cf. A., 1935, 581).—Vals. of $K\times10^5$, both classical and thermodynamic, have been obtained by the conductivity method for *m*- and *p*-methyl-, *m*-methoxy-, *o*- and *m*-fluoro-, *m*-bromo-, *o*- and *m*-iodo-, *m*- and *p*-nitro-benzoic acids, and *o*- and *m*-iodophenylacetic acids. The results are discussed. F. L. U.

Dissociation constants of polybasic acids. II. W. R. MAXWELL and J. R. PARTINGTON (Trans. Faraday Soc., 1936, **32**, 775—782; cf. A., 1935, 934).—The dissociation consts. of trimellitic, trimesic, mellophanic, prehnitic, and pyromellitic acids have been determined. The results support the hypothesis that the negative charge or charges on a dissociating ion produce an inhibiting effect which is a simple function of their no. and distance from the dissociating $\cdot CO_2H$. F. L. U.

Proton affinities of sparingly soluble bases: benzidine. E. B. R. PRIDEAUX and J. R. PARKINSON (Trans. Faraday Soc., 1936, **32**, 963—966).—The dissociation const. k_B, p_{k_1}, and p_{k_2} have been determined by colorimetric methods, by the electrometric method in aq. alcoholic solution and extrapolation to zero [EtOH], and colorimetrically in presence of solid base, giving, respectively, $k_B\times10^9$ 1·25, —, 1·74; p_{k_1} 5·097, 5·09, 5·23; p_{k_2} 3·61, 3·79, —. L. J. J.

Calorimetric study of the action of ammonia on cobalt chloride in water in presence of ammonium chloride. M. CHATELET (J. Chim. phys., 1936, **33**, 313—324).—Equilibria have been determined at 18° for the ions $Co(NH_3)^{\cdot\cdot}$ and $Co(NH_3)_3^{\cdot\cdot}$ previously detected (cf. this vol., 290). $Co^{\cdot\cdot}+NH_3 \rightleftharpoons Co(NH_3)^{\cdot\cdot}$ gives $K_1=[Co^{\cdot\cdot}][NH_3]/[Co(NH_3)^{\cdot\cdot}]=0{\cdot}3$ and $Co(NH_3)+2NH_3=Co(NH_3)_3^{\cdot\cdot}$ gives $K_2=[Co(NH_3)^{\cdot\cdot}][NH_3]^2/[Co(NH_3)_3^{\cdot\cdot}]=95$. Thus the equilibrium const. K_3, corresponding with the formation of $Co(NH_3)^{\cdot\cdot}$ from $Co^{\cdot\cdot}$, is $K_1K_2=28$. Heats of reaction have also been calc. M. S. B.

Ferric sulphate in aqueous solutions of other sulphates. F. K. CAMERON (J. Physical Chem., 1936, **40**, 689—696).—In general, addition of $Fe_2(SO_4)_3$ lowers the solubility of other sulphates. With $FeSO_4$ no double salt is formed between 25° and 50°. With $(NH_4)_2SO_4$ an alum is formed below 36°; the range of concn. in which it exists at 25° has been determined. With K_2SO_4 an alum is formed below 16° over a wide concn. range; above 16° $2K_2SO_4,Fe_2(SO_4)_3,14H_2O$ is stable at all but very high or very low concns. of $Fe_2(SO_4)_3$. E. S. H.

Lower cobalt sulphides. Equilibrium diagram of system Co–CoS. H. HÜLSMANN and F. WEIBKE [with K. MEISEL] (Z. anorg. Chem., 1936, **227**, 113—123; cf. A., 1935, 1335).—Thermal, microscopic, and X-ray analysis of the system Co–CoS confirms the results obtained by Friedrich (A., 1908, ii, 500). CoS melts at 1135±10°, and forms a homogeneous phase only in presence of a slight excess of S. The face-centred cubic lattice with a 9·924 A. characterises the γ-phase (Co_6S_5). F. L. U.

M.-p. diagram of boron trioxide–sodium metaborate melts. E. JENCKEL (Z. anorg. Chem., 1936, 227, 214—220; cf. A., 1935, 704).—The m.-p. diagram of the system B_2O_3–$NaBO_2$ affords evidence of the compounds $Na_2O,4B_2O_3$, $Na_2O,3B_2O_3$, and $Na_2O,2B_2O_3$. The two former exist in stable and unstable modifications. F. L. U.

System SO_3–H_2O and absolute sulphuric acid. E. Moles and C. R. de Robles (Anal. Fís. Quím., 1936, 34, 331—362).—The anomalous cryoscopic const. of H_2SO_4 (cf. Oddo *et al.* A., 1918, ii, 352) is supposed to be connected with the equilibrium $3H_2SO_4 \rightleftharpoons H_2SO_4,H_2O+H_2S_2O_7$. F. R. G.

Thermal dissociation of calcium carbonate. J. C. Southard and P. H. Royster (J. Physical Chem., 1936, 40, 435—438).—Measurements made with the use of a furnace in which a temp. of 900° could be maintained const. within 0·04° for over 30 hr. lead to pressures given by $\log_{10} p_{cm.} = -9140/T + 0{\cdot}382 \log_{10} T - 0{\cdot}668\times10^{-3}T + 9{\cdot}3171$. The temp. corresponding with 1 atm. is 894·4°. M. S. B.

Saturation pressure of ammonia in the thermal decomposition of zinc chloride diammine. E. Starokadomskaja (J. Appl. Chem. Russ., 1936, 9, 599—602).—The pressure of NH_3 over $ZnCl_2,2NH_3$ at 220—540° (1—40 atm.) agrees with that calc. from Krasnov's formula (Bull. All-Soviet Union Thermotech. Inst., 1935, No. 11). R. T.

Vapour pressure of nitric acid and ammonia over aqueous ammonium nitrate. V. A. Klevke and J. D. Chaskina (J. Chem. Ind. Russ., 1936, 13, 408—411).—The $[HNO_3]$ of the vapour from boiling aq. NH_4NO_3 is negligible for concns. $< 65\%$. The loss of NH_3 involved in concentrating a 60% solution (containing 0·5 g. of excess NH_3 per litre) to 93% amounts to 4·5—5 kg. per ton of solution. R. T.

Chemical transformations in ternary system copper–sulphur–oxygen. G. Sille (Metall u. Erz, 1935, 32, 270—283, 297—312; Chem. Zentr., 1935, ii, 1600).—The reactions undergone by the various binary systems involving Cu, CuO, Cu_2O, $CuSO_4$, and Cu_2S are considered. Reactions tending to the irreversible formation of Cu_2S and Cu_2O preponderate. J. S. A.

Three-component system CaO–Al_2O_3–H_2O. II. System rich in CaO. R. Nacken and R. Mosebach (Z. anorg. Chem., 1936, 227, 328—336).—The solubility of $3CaO,Al_2O_3,6H_2O$ (I) is 0·6820 g. per litre at 30°. The solid which first separates is $2CaO,Al_2O_3,7H_2O$, but, as the proportion of CaO increases, (I) is more readily formed and ultimately free $Ca(OH)_2$ is also present. It has not, so far, been possible to obtain the compound $4CaO,Al_2O_3,13H_2O$ under the conditions of these experiments. M. S. B.

Solubility equilibria of sodium sulphate at temperatures from 150° to 350°. II. Effect of sodium hydroxide and sodium carbonate. W. C. Schroeder, A. A. Berk, and A. Gabriel (J. Amer. Chem. Soc., 1936, 58, 843—849; cf. A., 1935, 1314).—Equilibrium data for the system Na_2SO_4–Na_2CO_3–H_2O at intervals of 50° from 150° to 350° have been determined. The existence of $Na_2CO_3,2Na_2SO_4$ has been established. The effect of adding NaOH to the ternary system has been examined. E. S. H.

Solubility in the system $ZnCl_2$–HCl–H_2O at 25°. D. I. Kuznetzov and A. A. Koshuchovski (J. Appl. Chem. Russ., 1936, 9, 185—188).—Solubility data at 25° are recorded. 60% of the Zn content of saturated aq. $ZnCl_2$ is pptd. as $2ZnCl_2,HCl,2H_2O$ on saturation with HCl. R. T.

Equilibria between water and the simple and double halides of cadmium and potassium. H. Hering (Ann. Chim., 1936, [xi], 5, 483—586).—Data for the systems KCl–$CdCl_2$–H_2O, KBr–$CdBr_2$–H_2O, and KI–CdI_2–H_2O (A., 1932, 469, 574; 1933, 906) are recorded. $KBr,CdBr_2,H_2O$ (I), $KBr,CdBr_2$, and KBr coexist with solution at 20·9° and (I)+KBr at −18·1°. Contrary to A., 1933, 906, $CdI_2,2KI,2H_2O$ (II) crystallises above −15·3° and $CdI_2,2KI,3H_2O$ below −15·3°. (II) and $CdI_2,2KI,0{\cdot}5H_2O$ (III) coexist at 81·4°. (III) exists above 76·3° but is decomposed by H_2O forming KI. J. G. A. G.

Ternary system manganese arsenate–arsenic acid–water. G. Grube, A. Heller, and W. Herrmann (Z. Elektrochem., 1936, 42, 223—226).—Four solid phases are indicated: $Mn_3(AsO_4)_2,H_2O$, $MnHAsO_4,4H_2O$, $H_4[Mn(AsO_4)_2],3H_2O$, and $H_4[Mn(AsO_4)_2]$. When H_3AsO_4 solutions containing $Mn^{\cdot\cdot}$ salts are electrolysed, it is found that $Mn^{\cdot\cdot}$ is gradually replaced by the complex Mn ions as the acid concn. is increased. C. R. H.

Behaviour of silver fluoride in complex formation. E. Hayek (Monatsh., 1936, 68, 29—32; cf. A., 1935, 1203).—AgI is sol. in conc. aq. AgF and yields a cryst. *compound* $AgI,AgF,2H_2O$. Migration experiments show the presence of a complex cation. AgBr behaves similarly, but the solubility of AgCl is only slightly increased. No reaction occurs with Ag_2O. F. L. U.

System dodecoic acid–sodium hydroxide–water. C. R. Bury and R. D. J. Owens (Trans. Faraday Soc., 1936, 32, 782—787; cf. A., 1935, 303).—Phase equilibria at 25° are shown in a triangular diagram. Solid phases in equilibrium with solutions on the alkaline side are $NaOH,H_2O$, anhyd. Na dodecoate (NaL), and curd (degree of hydration undetermined). In equilibrium with solutions on the acid side are HL, xNaL,yHL, and a liquid cryst. phase. The solubility of NaL is strongly depressed by NaOH and increased by HL. F. L. U.

Thermal potential of a mixture. J. E. Verschaffelt (Wis- en nat. Tijds., 1935, 7, 121—132; Chem. Zentr., 1935, ii, 1318—1319).—Theoretical. J. S. A.

Specific heat of gases as an aid in calculating equilibria. C. Schwarz (Arch. Eisenhüttenw., 1935—1936, 9, 389—396).—Mathematical. Expressions have been derived for the sp. heat and heat content at any temp. of H_2, O_2, CO, N_2, NO, OH, H_2O, CO_2, N_2O, CH_4, and C. A. R. P.

Heat capacity of saturated sodium sulphate solution. K. A. Kobe and C. H. Anderson (J. Physical Chem., 1936, 40, 429—433).—Over the range 32·4—102·8° the heat capacity is given by $C = 0{\cdot}803 - 1{\cdot}14\times10^{-4}t - 3{\cdot}2\times10^{-6}t^2$. The mean val. is 0·780 g.-cal. per g. of solution. The measured heat of

transition of $Na_2SO_4,10H_2O$ is 18,700, which agrees closely with the val. of 19,000 calc. from v.-p. data.
M. S. B.

Specific heat of hydrates of magnesium chloride. A. E. Aushbekovitsch (J. Appl. Chem. Russ., 1936, 9, 594—598).—On the basis of sp. heat measurements it is inferred that dehydration of $MgCl_2,6H_2O$ proceeds through the stages

$$[Mg,6H_2O]Cl_2 \rightarrow [Mg,4H_2O]Cl_2 \rightarrow [MgCl_2,2H_2O] \rightarrow [MgCl_2,2H_2O+MgCl_2]+[Mg,OH,Cl_2]H+ [MgO,MgCl_2]+MgCl_2 \rightarrow MgCl_2+MgO,MgCl_2.$$

R. T.

Calculation of activity coefficients. Electrolytic dissociation of nitric acid. O. Redlich and P. Rosenfeld (Monatsh., 1936, 67, 223—230).—Probable errors in the calculation of activity coeffs. from f.p. and e.m.f. data are discussed. Comparison of data for HNO_3 indicates that relatively large divergencies may be found for the vals. of the dissociation consts. and related quantities for strong electrolytes.
J. W. S.

Heat of formation and free energy of formation of boron nitride. S. Satoh (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 53—62).—The heat of formation of BN calc. from its v.p. and from the sp. heats of B, BN, and N_2 is 28,470 g.-cal., whilst $\Delta F_{298°}=54,760$ g.-cal.
R. S.

Thermochemistry of chloro-substituted benzoquinones and quinols. G. Sjöström (Svensk Kem. Tidskr., 1936, 48, 121—123).—Heats of combustion (kg.-cal.) at 20° (const. vol.) are: chloro- 619·4, 2 : 6-, 2 : 5-, and 2 : 3-dichloro- 584·8, 584·6, 583·9, trichloro- 549·6, and tetrachloro-benzoquinone 516·5, and for the corresponding -quinols 648·7, 610·0, 609·1, 611·8, 576·8, 545·0. The heats of reaction (reduction) of the above chlorobenzoquinones at 20° are respectively 38·8, 42·9, 43·6, 40·2, 40·9 (at 18°), 39·5.
E. P.

Activation energies of the addition of hydrogen halides to ethylene. C. E. Sun and C. Liu (J. Chinese Chem. Soc., 1936, 4, 98—101).—An attempt to calculate the affinity of C_2H_4 for HCl, HBr, and HI on the basis of activation energies. The calc. energies for the formation of EtCl, EtBr, and EtI are respectively 48·4, 39·0, and 31·5 kg.-cal.
C. R. H.

Measurement of conductivity of very dilute electrolytes. W. Grallert (Z. Elektrochem., 1936, 42, 330—336).—Errors are discussed, and portable apparatus suitable for laboratory use is described.
F. L. U.

Electrical conductivity, viscosity, and diffusion of certain lanthanum salts. L. W. Öholm (Soc. Scient. Fenn. Comm. Phys.-Math., 1936, 9, No. 2, 2—14).—Viscosities, determined by Ostwald's method, are in the order $La_2(SO_4)_3>LaCl_3>La(NO_3)_3$ at corresponding normalities. Redetermination of conductivities confirms substantially former results, $LaCl_3$ having slightly greater vals. than $La(NO_3)_3$ and $La_2(SO_4)_3$ much smaller vals. The diffusibilities increase with dilution in a similar way to that of the conductivities. The diffusion consts. are in the order $LaCl_3>La(NO_3)_3>La_2(SO_4)_3$.
D. C. J.

Cathodic current distribution in electrolytes. I. Zinc baths. E. Mantzell (Z. Elektrochem., 1936, 42, 303—315; cf. A., 1935, 306).—Current distribution (*D*) at the cathode has been studied under varying conditions in six different types of Zn-plating bath. In all types the effect of increasing c.d. is unfavourable. Some improvement results by decreasing $[Zn^{\cdot\cdot}]$ whilst the conductivity (κ) is const., and in acid baths by increasing κ by the addition of NH_4 salts. Under given conditions, cyanide baths show the best *D*, that in alkali zincate baths being relatively poor despite their high κ. The distribution of metal at the cathode follows *D* closely in acid baths, in which the current yield approaches 100%, but is more uniform than *D* in zincate and cyanide baths.
F. L. U.

Transport numbers of paraffin-chain salts in aqueous solution. I. Measurement of transport numbers of cetylpyridinium and cetyltrimethylammonium bromides and their interpretation in terms of micelle formation, with data for cetanesulphonic acid. G. S. Hartley, B. Collie, and C. S. Samis (Trans. Faraday Soc., 1936, 32, 795—815; cf. A., 1935, 299).—The transport nos. (*T*) of the two paraffin-chain cations increase rapidly with increase of concn. in the range where the total equiv. conductivity (λ) falls, finally becoming $\gg 1$. In the first part of this range the increase of *T* is so great that the λ of the cation is $>$ its val. at infinite dilution, thus demonstrating the formation in this range of mobile micelles. The accompanying decrease of total λ is due to a braking effect caused by adherence to the micelles of Br' ions, the mean mobility of which is negative over a considerable range of concn. The increase of total λ observed at moderate concns. is due, not directly to formation of more mobile micelles from less mobile simple ions, but to the liberation of compensating ions previously attached to the micelles. An approx. estimate of the size of the micelles is given.
F. L. U.

Faraday's law and electrolysis by spark. P. Jolibois and P. de Beco (Compt. rend., 1936, 202, 1496—1498; cf. A., 1935, 837).—If diffusion of the acid which is formed at the positive pole is prevented the quantity of oxide formed agrees with Faraday's law.
R. S.

Bismuth electrode. A. Holmqvist (Svensk Kem. Tidskr., 1936, 48, 106—120).—On varying $[Bi^{\cdot\cdot\cdot}]$ in aq. HCl, H_2SO_4, and $HClO_4$ free from air, the potential changes in accordance with Nernst's formula. The p.d. between a normal H_2 electrode and a Bi electrode in 1*M*-$Bi^{\cdot\cdot\cdot}$ is 0·289 volt.
E. P.

Behaviour of the cadmium electrode in alkaline nickel–cadmium accumulators. G. Grube and E. Doetsch (Z. Elektrochem., 1936, 42, 247—258).—Changes in terminal voltage, in the single electrode potential, and in the electrolyte during the charge and discharge of Ni–Cd accumulators have been studied. The behaviour of Cd electrodes which contain 14·6% of Fe_3O_4 has been compared with that of pure Cd electrodes prepared in various ways.
C. R. H.

Calculation of normal potential of metals and Henry constant of ions. I. Uhara (Phil. Mag., 1936,

[vii], 21, 958—976).—Normal potentials of metals in H_2O and non-aq. solvents are deduced thermodynamically. Calc. and experimental vals. are compared. There is a parallelism between the Henry const. and the heat of hydration of ions. H. J. E.

Electrometric potential and concentration of electrolytes. (Mlle.) S. Veil (Compt. rend., 1936, 202, 1665—1666).—If π_σ is the e.m.f. of saturated aq. $CuCl_2$ of concn. σ and π at concn. c, then $\pi=\pi_\sigma(c/\sigma)^k$ where k is approx. $\frac{1}{6}$ for the concn. range σ—$\sigma/10{,}000$ at room temp. M. S. B.

Thermodynamical exposition of the operation of reversible gas electrodes. J. W. H. Lugg (J. Proc. Austral. Chem. Inst., 1936, **3**, 126—130).—Theoretical. The significance of the metal holding the gas is discussed, and a theory of single electrode potential, in which the characteristics of the electrode metal are considered, is formulated. E. S. H.

Physical significance of activity coefficients in reversible electrode equilibria. J. W. Belton (Phil. Mag., 1936, [vii,] **21**, 1140—1144).—A relationship is derived between the activity coeff. of an electrolyte and the p.d. between this electrolyte and the region where ion-neutralisation occurs (adsorption potential). J. W. S.

Influence of p_H on the Becquerel effect of coloured electrodes. (Mlle.) C. Stora (Compt. rend., 1936, 202, 1666—1668).—Dark potentials and photopotentials of oxidation–reduction indicators, such as Nile-blue and methylene-blue, and of derivatives of xanthane, CH_2Ph_2, and $CHPh_3$, have been determined. The rules which govern the influence of p_H on the Becquerel effect for electrodes in metallic salts do not, in general, appear to apply to coloured electrodes. Apart from catalysis of the photochemical reaction at the electrode by OH′, it is necessary to consider the variation with p_H of the absorption of the photosensitive compound and also to use monochromatic light in the experiments. M. S. B.

Capillary-electric phenomena in molten salts. S. Karpatschov and A. Stromberg (Z. physikal. Chem., 1936, **176**, 182—186).—The electrocapillary curves of Sn, Pb, Cd, and Tl in contact with molten KCl–LiCl and KI–LiI mixtures and with molten Pb as auxiliary electrode have been determined. The p.d. of the max. on the curve for a given electrolyte varies considerably according to the metal with which it is in contact. From the curves for Sn the capacity, C, of the double layer as a function of the polarising voltage has been determined. The val. of C corresponding with the equilibrium potential of Sn in both electrolytes is 90—100 μF per sq. cm. R. C.

Electromotive force of movement of metals in water and their electrokinetic potential. S. Procopiu (Compt. rend., 1936, 202, 1371—1373; cf. A., 1930, 546).—For various metals the e.m.f. decreases with time in pure H_2O, but is const. in sucrose solution, and is of the same magnitude and sign as the elektrokinetic potential. The influence of velocity and of the dielectric const. of the liquid has been studied. R. S.

Hydroelectric and contact cells. (Mlle.) S. Veil (Bull. Soc. chim., 1936, [v], 3, 860—865).—When Pt is placed in contact with other metals in gelatin the e.m.f. vals. obtained are: Zn 1·01, Cd 0·72, Fe 0·59, Pb 0·54, Ni 0·28, Cu 0·22 volt. The relative importance of Volta effect and chemical action in electrolytic cells is discussed. E. S. H.

Study of the cryolite–aluminium oxide cell with particular reference to decomposition voltage. J. W. Cuthbertson and J. Waddington (Trans. Faraday Soc., 1936, 32, 745—760).—At 1025° the decomp. voltages of cryolite and of cryolite with Al_2O_3 (16%) are respectively 2·23 and 2·20 volts with Pt, and 1·7 and 1·5 volts with graphite, anodes. The decomp. voltage of cryolite falls nearly linearly with rising temp. In the Al cell the current is carried by the cryolite. The Al_2O_3 is only slightly, if at all, ionised, and functions as both a cathodic and anodic depolariser, supplying Al at the cathode and regenerating AlF_3 at the anode. F. L. U.

Mechanism of the decomposition of aluminium–magnesium solid solutions. P. Lacombe and G. Chaudron (Compt. rend., 1936, 202, 1790—1792; cf. B., 1935, 678).—The dissolution potential of a quenched Mg–Al solid solution (9% Mg), after annealing below 280°, increases at first with time of annealing but later decreases almost to its initial val. The velocity of attack by acid of fixed concn. shows a corresponding max. This is interpreted as indicating that the constituent initially pptd. is unstable and richer in Mg than the compound Al_3Mg_2. J. W. S.

Passivity of chromium. IV. Electromotive behaviour of chromium amalgam. E. Müller (Z. physikal. Chem., 1936, **176**, 273—288; cf. A., 1932, 473).—In M-HCl at 20°, Cr amalgam oscillates periodically between the active and passive states, a phenomenon which is ascribed to the simultaneous occurrence of the processes $Cr \rightarrow Cr^{\cdot\cdot}+2\ominus$, $2\ominus+2H^{\cdot}=H_2$, the second of which tends to reduce the electrode potential below the val. required for the first. In M-H_2SO_4 massive Cr is passive but can be permanently rendered active by weak cathodic polarisation. Cr amalgam is rendered active temporarily by polarisation, but becomes active on shaking. In M-$HClO_4$ the behaviour is similar, except that shaking does not cause activation. In all three acids the amalgam is rendered passive by strong cathodic polarisation. The activation potentials in the various acids are < for massive Cr, but form the same sequence. The experimental results are incompatible with Müller's coating theory of passivity. R. C.

Measure of acidity obtained from the electromotive force of a cell without liquid junction. D. I. Hitchcock (J. Amer. Chem. Soc., 1936, 58, 855—856).—The product $m_H\gamma_H\gamma_{Cl}$ is regarded as a promising measure of acidity in preference to p_H. E. S. H.

Reduction potentials of organic systems. I. Bimolecular reduction of thioindigotindisulphonate. A. E. Remick (J. Amer. Chem. Soc., 1936, 58, 733—736).—The reduction potential (E'_0) of the system thioindigotindisulphonate–leuco-compound at p_H 2·02—7·61 and 25° varies linearly with the concn. of the oxidant [$K_3Fe(CN)_6$] at const. % oxidation. The results conform to the thermodynamic equations for a one-step bimol. reduction involving 1*e* per mol. of dye. H. B.

Oxidation–reduction potential of α-aminoketobutyric ester and of reductone.—See this vol., 888.

Brönsted's kinetic equation and the Debye theory. II. A. Musil (Monatsh., 1936, **67**, 269—319; cf. A., 1932, 1209).—Anomalies in the Debye theory are eliminated by application of the Brönsted equation, enabling the theory to be applied to reaction kinetic problems. The author's theory is supported by experimental data for the hydrolysis of esters of AcOH by alkali carbonates and hydroxides in presence of KCl, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, and K silicotungstate. J. W. S.

Reactions produced by adiabatic expansion in systems in chemical equilibrium. P. Montagne (Compt. rend., 1936, **202**, 1430—1432).—Theoretical. L. J. J.

Kinetics of recombination of bromine atoms. II. E. Rabinowitch and W. C. Wood (Trans. Faraday Soc., 1936, **32**, 907—917; cf. A., 1935, 586).—The authors' optical method has been used to measure the stationary [Br] in illuminated Br_2 vapour, and velocity coeffs. for three-body recombination in presence of He, A, H_2, N_2, O_2, CH_4, and CO_2 have been determined. The recombination rate of Br is 2—3 times $<$ that of I with the same third body. The results in mixtures and in pure Br_2 agree with theory. L. J. J.

Oxidation of silicon hydrides. II. H. J. Emeléus and K. Stewart (J.C.S., 1936, 677—684; cf. A., 1935, 1207).—The lower crit. explosion pressures (P_l) of mixtures of O_2 with SiH_4, Si_2H_6, and Si_3H_8 and the upper crit. explosion pressures (P_u) for mixtures of O_2 with Si_2H_6 and Si_3H_8 have been studied as a function of the composition of the gas mixture and diameter of the glass explosion vessel. P_l is lowered and P_u raised by rise of temp. The inflammability of these compounds increases with increasing at. wt. The results are in accord with chain mechanisms analogous to that previously suggested for SiH_4. J. W. S.

Influence of pressure on the spontaneous ignition of inflammable gas–air mixtures. IV. Methane–, ethane–, and propane–air mixtures. D. T. A. Townend and E. A. C. Chamberlain (Proc. Roy. Soc., 1936, **A**, **154**, 95—112; cf. A., 1934, 151, 1179).—The influence of pressure up to 30 atm. on the ignition temp. of CH_4–, C_2H_6–, and C_3H_8–air mixtures has been determined. With CH_4–air mixtures the ignition points are confined to an upper range even at pressures up to 30 atm. With C_2H_6–air mixtures, a lower-temp. ignition system develops at pressures $>$ 13 atm.; 1% of MeCHO, however, produces a reduction of this to $<$ 5 atm. C_3H_8–air mixtures show all the ignition features of the higher paraffins, ignition in the lower system being facilitated by the presence of MeCHO or EtCHO. The influence of pressure on pre-ignition time-lags has been investigated. L. L. B.

Initial formation of alcohols during the slow combustion of methane and ethane at atmospheric pressure. D. M. Newitt and J. B. Gardner (Proc. Roy. Soc., 1936, **A**, **154**, 329—335).—During the slow combustion of CH_4 and C_2H_6 at atm. pressure MeOH and EtOH, respectively, are formed in quantities comparable with those of the corresponding aldehydes. Both alcohols and aldehydes are found during the induction period, but the ratio alcohol : aldehyde diminishes as the induction nears completion. The results prove that the formation of alcohol precedes that of the corresponding aldehyde. L. L. B.

Slow combustion of methane, methyl alcohol, formaldehyde, and formic acid. W. A. Bone and J. B. Gardner (Proc. Roy. Soc., 1936, **A**, **154**, 297—328).—The induction period in the slow combustion of CH_4 at 390—420° is (*a*) uninfluenced by separately pre-heating the reactants or exposing the reacting medium to ultra-violet light; (*b*) lengthened by increasing the surface/vol. ratio of a SiO_2 reaction vessel; (*c*) shortest with a $2CH_4+O_2$ medium; (*d*) characterised by the successive formation of small equilibrium amounts of MeOH and CH_2O; (*e*) shortened by previous small additions of NO_2, but lengthened by addition of I. No peroxide was detected during the induction period. Under similar conditions, the slow oxidation of MeOH is much faster and less influenced by SiO_2 surface than is that of CH_4 at 390°. There is no appreciable induction period, although the reaction is accelerated by small additions of CH_2O or NO_2. The most reactive medium is $2MeOH+O_2$. The oxidation is marked by the intermediate successive formations of CH_2O and HCO_2H, and the end products are chiefly oxides of C and steam, with a high CO/CO_2 ratio. In the slow combustion of CH_2O, no induction period is observed even at 275°, and the speed of the reaction is much $>$ that of either MeOH or CH_4. HCO_2H is formed intermediately, together with performic acid (I) and "formaldehyde peroxide" (II), the latter being dependent on the prior formation of (I). The end products are again chiefly oxides of C and steam, with a high CO/CO_2 ratio. Fair amounts of H_2 are formed, probably from the decomp. of (II). Experiments made on the reactions of both 2 : 1 and 1 : 1 HCO_2H/O_2 mixtures between 340° and 470° showed a slower disappearance of O_2 than thermal decomp. of HCO_2H. The gaseous products are chiefly CO, CO_2, H_2O, and H_2, and there is no intermediate formation of a peracid or peroxide. The results all fit the hydroxylation theory. L. L. B.

Slow combustion of formaldehyde. R. Spence (J.C.S., 1936, 649—657).—CH_2O reacts rapidly with O_2 in Pyrex vessels at 317°. In unpacked vessels of $\nless$ 1 mm. diameter the chief products are CO and H_2O but in vessels packed with powdered glass combination to form CO_2 is complete. From the kinetics of the reaction a chain mechanism is proposed. J. W. S.

Primary process in the thermal decomposition of formaldehyde and formic acid. F. Patat and H. Sachsse (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., III, 1935, [ii], **1**, 41—48; Chem.

Zentr., 1935, ii, 1526; cf. A., 1935, 708).—The decomp. in the presence of para-H_2 is studied. Since exchange is not observed it is concluded that the primary process involves saturated mols., contrary to the radical chain theory of Rice and Herzfeld (A., 1934, 369). H. N. R.

Mechanism for the decomposition of ethylene oxide. D. V. Sickman (J. Chem. Physics, 1936, **4**, 297—299).—Theoretical. The kinetic data of Heckert and Mack (A., 1929, 1243) are in qual. agreement with an initial isomerisation to MeCHO, accompanied by a reaction producing free radicals which induce a chain decomp. of the MeCHO. L. J. J.

Thermal decomposition of acetaldehyde and ethylene oxide.—See this vol., 825.

High-temperature pyrolysis of gaseous olefines.—See this vol., 818.

Thermal decomposition of ethylene oxide.—See this vol., 820.

Mechanism of flame extinction by carbon tetrachloride.—See B., 1936, 482.

Theory of detonation.—See B., 1936, 525.

Kinetics of thermal *cis–trans*-isomerisations. V. G. B. Kistiakowsky and W. R. Smith (J. Amer. Chem. Soc., 1936, **58**, 766—768).—With Δ^{β}-butene the reaction is of approx. first order, but of second order with respect to initial pressure. A chain mechanism is suggested. The equilibrium composition at 633° and 620° abs. is 52·8% of *trans*-isomeride. E. S. H.

Magnitude of radical concentration in homogeneous thermal decomposition of organic molecules. I. Calculation of radical concentrations found by the para-hydrogen method, and the reaction CH_3+H_2. II. Radical concentration in decomposition of dimethyl ether and propane. F. Patat (Z. physikal. Chem., 1936, **B**, **32**, 274—293, 294—304).—I. Partly a more detailed account of work previously described (this vol., 293). From observations of the photochemical decomp. of MeCHO the ratio k_1/k_2 is found to be $0{\cdot}001e^{-(1870\pm900)/RT}$. For $Me+H_2\rightarrow CH_4+H$ (I) there is a steric factor of $\sim10^{-4}$ and the energy of activation is $\ngtr$ 9 kg.-cal. The *p*-H_2 transformation in the photochemical decomp. of MeI and $COMe_2$ observed by West (A., 1935, 1468) is not of paramagnetic nature, but is ascribed to H atoms formed by (I). The heat of formation of CH_4 from Me+H is $\nless$ 103 kg.-cal.

II. The stationary [H] and [Me] in the thermal decomp. of Me_2O and C_3H_8 have been determined. A review of all the available experimental data shows that in all the thermal decomp. in which the Rice–Herzfeld theory requires a chain mechanism radicals are actually formed, but in concns. so small as to be quite inadequate for the total decomp. by chains. In the homogeneous thermal decomp. of the org. mols. studied the first step is decomp. into saturated fragments, and the requisite energy of activation is < the linking energy of the weakest linking. R. C.

Kinetic correlation of two reactions involving hydrogen peroxide. Its oxidation by chloramine-*T* and by chlorine. H. A. Liebhafsky (J. Amer. Chem. Soc., 1936, **58**, 705—707).—Theoretical. A mechanism for the oxidation of H_2O_2 by chloramine-*T*, based on published results, is advanced. E. S. H.

Velocity of diazotisation. K. Rostovceva (Z. anal. Chem., 1936, **105**, 32—35).—The velocity of diazotisation of aromatic amines, relative to that of benzidine (I), is determined by mixing a solution of the amine with an equal vol. of 0·1*N*-(I), both in conc. HCl. 0·1*N*-$NaNO_2$ is added at 5°, and after 15—20 min., (I) sulphate is pptd. by adding Na_2SO_4, and is determined volumetrically. It is proposed to employ the method for analysis of mixtures of isomeric amines. J. S. A.

Glycoside fission in non-aqueous media. I, II.—See this vol., 827.

Reactivity of halogen compounds. II. Rates of reaction and energies of activation of 1 : 2 : 4-chlorodinitrobenzene with aromatic primary amines. A. Singh and D. H. Peacock (J. Physical Chem., 1936, **40**, 669—678; cf. A., 1935, 1465).—The velocities of reaction of 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ with NH_2Ph, *o*-, *m*-, and *p*-$C_6H_4Me{\cdot}NH_2$, *m*- and *p*-$C_6H_4Cl{\cdot}NH_2$ and -$C_6H_4Br{\cdot}NH_2$, *o*-, *m*-, and *p*-anisidine, and α- and β-$C_{10}H_7{\cdot}NH_2$ (0·4 and 0·8*M*) have been determined at 35° and 45°, and the energies of activation calc. The effect on the energy of activation of transferring a substituent from the *m*- to the *p*-position is as predicted by the Lapworth–Robinson hypothesis. The changes in energy of activation have been compared with the dipole moments. E. S. H.

Mode of action of solvents on chemical reaction velocity. C. N. Hinshelwood (Trans. Faraday Soc., 1936, **32**, 970—972).—Theoretical. The rate of an association reaction in solution may be determined by deactivation of the product by solvent mols. The kinetic phenomena resulting from such a mechanism are discussed. L. J. J.

Inversion of sucrose in mixtures of light and heavy water. P. Gross, H. Steiner, and H. Suess (Trans. Faraday Soc., 1936, **32**, 883—889).—The rate of inversion of sucrose in H_2O–D_2O mixtures containing H_2SO_4 at 25° increases with the D_2O content, but not linearly. The effect is due to an increase in concn. of reacting complexes, the theory of which is discussed and shown to account for the effect with Et diazoacetate. L. J. J.

Depolymerisation of water by capillarity and the inversion of sucrose. E. Toporescu (Compt. rend., 1936, **202**, 1672—1674).—The e.m.f. of a Pt–Ni couple in H_2O is changed if one of the electrodes is placed in capillary H_2O. This is attributed to depolymerisation of the H_2O in the capillary. By dialysis of aq. sucrose (I) through parchment-paper the rate of inversion of (I) is increased. On the assumption that depolymerisation of H_2O takes place in the capillaries of a porous body, this result is in agreement with an earlier observation that depolymerisation of H_2O by NaCl also increases the rate of inversion of (I) (cf. A., 1932, 346). M. S. B.

Substitution and inversion of configuration. E. Bergmann, M. Polanyi, and A. L. Szabo (Trans. Faraday Soc., 1936, **32**, 843—852; cf. A., 1933, 574).—The rate of racemisation of $CHMePr^{\alpha}I$ and $CHMeBu^{\alpha}I$ by I′ ions has been compared with the rates of exchange between halogens in related compounds. For the racemisation, *k* follows the Arrhenius equation with a temp.-independent factor of approx. 10^{10}, and the *k* vals. for any set of analogous substitution or racemisation reactions form a continuous series. L. J. J.

"Activated complex" theory and the influence of solvents on reaction velocity. S. Glasstone (J.C.S., 1936, 723—724).—From the activated complex theory of reaction velocities (A., 1935, 827, 1205) it is deduced that association of reactant mols., but not of the activated complex, should increase reaction velocity (*v*), whereas association of the activated complex and not of the reactants should decrease *v*. Compound formation between one or both reactants and the solvent should also decrease *v*. J. W. S.

Thermal decomposition of sodium and potassium azides. W. E. Garner and D. J. B. Marke (J.C.S., 1936, 657—664).—The thermal decomp. of KN_3 in K vapour is very much more rapid than in a vac., but that of NaN_3 is only slightly catalysed by Na vapour. Microscopical examination of partly decomposed crystals shows that reaction begins on the surface and along lines, probably cracks in the crystal, but that with KN_3 in a vac. reaction later penetrates to the interior. The energies of activation of KN_3 and NaN_3 are 36·1 and 34·4 kg.-cal., respectively. Comparison with other azides indicates that there is no relationship between sensitivity and activation energy. J. W. S.

Kinetic investigations by means of the photoelectric cell of the decomposition of sodium mercury sulphide by water and of sodium tungstate by excess of strong acids. A. Lottermoser and G. von Hessling (Kolloid-Z., 1936, **75**, 184—192).—Technique for determining the rate of formation of a sol by turbidity measurements is described. The influence of concn. of reagents has been investigated. E. S. H.

Decomposition of ferrous oxide. J. Bénard and G. Chaudron (Compt. rend., 1936, **202**, 1336—1338; cf. A., 1924, ii, 617).—The rate at 350—480°, measured by the change in magnetic properties, $\propto [FeO]^8$. The reaction is $8FeO = Fe_3O_4 +$ a solid solution (Fe,4FeO). Formation of the solid solution is shown by an increase in the parameter of FeO, measured by *X*-rays, as the reaction progresses. Above 480° the order of the reaction decreases regularly. H. J. E.

Pyrolysis of chlorates and perchlorates. I. M. Crespí and J. L. G. Caamaño (Anal. Fís. Quím., 1936, **34**, 320—326).—Apparatus for measuring the initial decomp. temp. and velocity of evolution of gas during the pyrolysis is described. Data are given for the pyrolysis of $KClO_3$ and $KClO_4$ with or without addition of SiO_2 and KCl. The pyrolysis is autocatalytic. F. R. G.

Investigation of [thermal] decomposition of [solid] barium oxalate by emanation method. B. Sagortschev (Z. physikal. Chem., 1936, **176**, 295—302).—The progress with rise of temp. of the decomp. to give $BaCO_3$ of various preps. with admixed Th-*X* has been followed by observing the emanating power, *E*. With loss of CO *E* increases owing to increase in the surface of the crystal. A rise in *E* above 500° is apparently due to a loosening of the crystal resulting in increased mobility of its component units. R. C.

Reaction chain in thermal denaturation of proteins. A. Fischer (Z. physikal. Chem., 1936, **176**, 260—272).—A study of the denaturation of serum-globulin and ovalbumin at 70° has shown that the mechanism is identical with that of the coagulation of blood (cf. A., 1935, 1143). There is first produced a reactive form of protein, which then promotes denaturation, apparently by a chain mechanism. If a portion of a solution of a protein in which denaturation has set in is added to a fresh solution at 70° denaturation starts there at once. Denaturation probably comes about by groups anchored at lower temp. within the globular protein mol. coming up to the surface in some of the mols. due to the shift of equilibrium with temp., whereupon all the protein mols. orient themselves by a reorganisation of their surface groupings. This view is supported by the observations that denaturation can be suppressed by causing all the NH_2 groups to react with CH_2O, and that heparin reacts with denatured proteins (cf. *ibid.*, 1002). R. C.

Water-line corrosion.—See B., 1936, 501.

Reactions involving proton transfers. R. P. Bell (Proc. Roy. Soc., 1936, **A**, **154**, 414—429).—The step determining the rate of a reaction involving general catalysis by acids or bases is the transfer of a proton from catalyst to substrate, or vice versa. Brönsted's equation relating acid–base dissociation consts. to catalytic power is generalised to include the case in which the catalyst remains the same and the substrate varies. Equations are given for the rate at which a stream of particles in temp. equilibrium pass an unsymmetrical parabolic potential barrier, taking into account the "tunnel effect." Application of these to the present problem shows that the deviations from classical behaviour will be considerable, and that a linear relation between dissociation energy and activation energy will still lead to the Brönsted equation, but not to a simple relation between the apparent activation energy and the reaction velocity. L. L. B.

Catalysis and inhibition of a homogeneous gas reaction. Influence of nitric oxide on the decomposition of diethyl ether. L. A. K. Staveley and C. N. Hinshelwood (Proc. Roy. Soc., 1936, **A**, **154**, 335—348).—Small quantities of NO inhibit the normal decomp. of Et_2O, a min. in the rate being observed with about 1—2 mm. of NO. Larger amounts, however, catalyse the decomp., the catalysis resembling that caused by I in that the activation energy is < that of the normal reaction and is distributed in two square terms only. The residual reaction occurring in presence of NO has an activation energy of 67,000 g.-cal. These must be distributed in 18 square terms (9 degrees of freedom) to explain the observed rate. There is no difference between the dependence of rate on [Et_2O] in the inhibited and uninhibited reactions. A theory involving the existence of short chains is advanced to explain the results. L. L. B.

Honogeneous catalytic oxidation of benzene. R. H. Griffith and S. G. Hill (Trans. Faraday Soc., 1936, **32**, 829—836).—The homogeneous oxidation of C_6H_6 vapour has been studied at about 430° using $EtNO_3$ as a catalyst. A linear relationship is found between (1) time of half change (T) and [$EtNO_3$], (2) $1/T$ and the ratio O_2/C_6H_6, (3) $1/T$ and total pressure, (4) T and 1/abs. temp. The relationship is direct for (2), (3), and (4), and inverse for (1). With $> 0{\cdot}35\%$ of $EtNO_3$ the reaction is explosive. Increase of surface (Pyrex glass) causes retardation, as does the introduction of $PbEt_4$. The results are discussed. F. L. U.

Decomposition of diazoacetic ester catalysed by protons and deuterons. P. Gross, H. Steiner, and F. Krauss (Trans. Faraday Soc., 1936, **32**, 877—879).—At 0° the hydrolysis is $\sim$ 3 times as rapid in pure D_2O as in pure H_2O. In mixtures the increase in rate is not a linear function of the D content. L. J. J.

Effect of propyl alcohol on the hydrolysis of sulphuric acid esters. K. H. Bauer and W. Poethke (Fettchem. Umschau, 1936, **43**, 69—71; cf. A., 1930, 1019).—Octadecylsulphuric acid (I) is readily hydrolysed by aq. HCl or H_2SO_4, but more slowly than is ricinoleosulphuric acid (II); the addition of PrOH to the reaction mixture reduces the speed of hydrolysis to a very marked degree in the case of (I) (but does not completely check it) and to a smaller extent in the case of (II). The difference in the hydrolytic behaviour of the two esters is quant. and not qual. as supposed by Seck (A., 1934, 604). E. L.

Optical activity in relation to tautomeric change. VI. Comparison of the rates of racemisation and of bromination of a ketone. Further study under conditions of basic catalysis. S. K. Hsü and C. L. Wilson (J.C.S., 1936, 623—625; cf. A., 1934, 849).—The rates of bromination and racemisation of *d*-2-*o*-carboxybenzylindan-1-one in AcOH solution with NaOAc as catalyst are both unimol. and have comparable velocity coeffs. J. W. S.

Santene inversion of fenchyl alcohol and its conditions.—See this vol., 856.

Induced oxidation in which ascorbic acid among others is the inductor. W. P. Jorissen and A. H. Belinfante (Rec. trav. chim., 1936, **55**, 374—378).—Data for the induced oxidation of lactic acid (I) and arsenite solutions (II) by glycuronic and ascorbic acids show that (I) and (II) absorb approx. the same amount of O_2 as the inductor. C. R. H.

Catalysed reaction of magnesium ethyl bromide with ethyl bromide.—See this vol., 830.

Action of bromine on acetone in presence of various solvents.—See this vol., 825.

Oxidase-like action of certain complex metal salts. Y. Shibata and K. Shibata (Iwata Inst. Plant Biochem., Publ. 2, 1936, 1—9).—About 60 complex ammines of Co, Ni, Fe, Zn, Cd, Cu, Cr, and Ag have been classified according to their catalytic activity towards oxidation reactions. Myricetin (I) was used as an oxidation indicator. The oxidising activity of a catalyst appears to be in inverse ratio to its stability in aq. solution. All the Cr, Fe, and Ag compounds examined, with one Cd and some Co compounds, are inactive. Certain factors inhibiting the action of oxidase have a similar influence on active complex metal salts. These are the increased acidity of the medium, the action of certain enzyme poisons such as KCN, $HgCl_2$, NH_2OH, etc., preliminary heating of the catalyst, and preliminary treatment of (I) with an inactive complex salt. It is suggested that the oxidation takes place through the medium of H_2O and that the action of the catalyst, whether oxidase or metal complex, is to increase the reactivity of the H_2O towards the substrate through combination with both mols. by co-ordinate linkings. It is also suggested that the active nucleus of an oxidase is a metal complex. M. S. B.

Kinetics of the oxidising action of certain complex metal salts. Y. Shibata and H. Kaneko (Iwata Inst. Plant Biochem., Publ. 2, 1936, 10—31).—The catalytic action of complex Co salts on the oxidation of pyrogallol (I) has been studied. The activity diminishes in the order purpureo- > roseo- > xantho-salts, the activity of the last being very small or zero. This is also the order in which reactivity with H_2O diminishes (cf. preceding abstract). After an induction period of varying length the reaction is unimol. For $0{\cdot}004M$-(I) the optimum concn. of complex salt is approx. $0{\cdot}002M$. At concn. c of catalyst $< 0{\cdot}002M$ $k_1/k_2=(c_1/c_2)^{0{\cdot}1}$. The temp. coeff. of k increases with increasing inactivity of the catalyst so that, at high temp., it approaches the same val. for the three groups of salts. Inhibitors act as previously described for other catalysed oxidations (*loc. cit.*). M. S. B.

Decomposition of hydrogen peroxide by complex metal salts. Y. Shibata and H. Kaneko (Iwata Inst. Plant Biochem., Publ. 2, 1936, 32—39).—The catalytic decomp. of H_2O_2 by $[Ni(NH_3)_6]Cl_2$ and $[Cu(NH_3)_4]Cl_2,H_2O$ is unimol. and similar to that brought about by catalase or Pt sol. k depends on [$H^{\cdot}$] and is a max. in feebly alkaline solution. k also depends on the concn. c of the complex salt and $k_1/k_2=(c_1/c_2)^{1{\cdot}3}$. The mean val. of the temp. coeff. for 10° is 1·77. $HgCl_2$, KCN, $KClO_3$, and $K_4Fe(CN)_6$ act as catalyst poisons. M. S. B.

Oxidising action of colloids. I. Oxidation with colloidal metals. Y. Shibata and H. Kaneko. **II. Oxidation with colloidal metal hydroxides and silicates.** H. Kaneko (Iwata Inst. Plant Biochem., Publ. 2, 1936, 40—54, 55—73).—I. The catalytic oxidation of pyrogallol in presence of Ag, Au, Cu, Hg, Bi, Sb, and Pt sols has been followed by measurements of the extinction coeff. with the spectrophotometer. The reaction is unimol. For dil. Pt sols the connexion between k and concn. c of the sol. is $k_1/k_2=(c_1/c_2)^{0{\cdot}35}$ and the temp. coeff. is 1·21 per 10°. At 40—45° the reaction begins to show irregularities.

II. The oxidation of pyrogallol is catalysed by colloidal hydroxides of Ti, Cr, Fe^{III}, Mn^{II}, Ni, Co, Cu, Zn, and Al, and by Mg (I), Al, and various natural colloidal silicates. The reaction is of the first order. (I) gives $k_1/k_2=(c_1/c_2)^{0{\cdot}45}$ and a temp. coeff. of 1·24 per 10° below 40°. Addition of a complex metal salt with no catalytic power alone, $[Co(NH_3)_3(NO_2)_3]$ or $[Cr(NH_3)_5Cl]Cl_2$ increases, to a remarkable extent, the catalytic action of colloidal metal hydroxides and especially of colloidal silicates. M. S. B.

Catalytic oxidising action of colloids. Y. Shibata and K. Tamasaki (Iwata Inst. Plant Biochem., Publ. 2, 1936, 201—206).—The influence on O_2 absorption by pyrogallol (I) of certain metal sols, previously shown by a spectro-photometric method to catalyse the oxidation of (I), has been examined. Pt sol causes a marked absorption of O_2 which varies with the method of prep. of the sol, but Ag and Au sols produce no appreciable absorption. M. S. B.

Iodide oxidation by complex metal salts. A. Watanabe (Iwata Inst. Plant Biochem., Publ. 2, 1936, 74—87).—The catalytic oxidation of KI by Co ammines is parallel with the influence of the latter on pyrogallol oxidation. The p_H of the solution rises during the reaction, but this rise may be prevented by the use of buffers, and the buffered reaction is unimol. The optimum p_H for the reaction is approx. 6. The behaviour of the ammines is similar to that of iodide-oxidases. The dependence of k on ammine concn. is expressed by $k_1/k_2=(c_1/c_2)^{0{\cdot}36}$. For const. ammine concn. k falls with diminution of initial [KI]. Determination of k for temp. 0—30° showed that a rapid increase takes place between 10° and 20°. M. S. B.

Catalytic action of complex metal compounds. K. Shibata and A. Watanabe (Iwata Inst. Plant Biochem., Publ. 2, 1936, 97—128).—The formation of indophenol from Nadi reagent (p-$NH_2{\cdot}C_6H_4{\cdot}NMe_2$ and α-$C_{10}H_7{\cdot}OH$) has been employed in further investigations on the oxidising action of complex metal salts (cf. preceding abstracts). *m*-Phenols, which are not oxidisable, inhibit the oxidation of *o*- and *p*-phenols, probably by attaching themselves to the metal complex in place of the latter. Certain complexes can oxidise only in presence of H_2O_2 and so behave like peroxidase. The accelerating action of these compounds on the catalytic oxidation by active ammines is due to the presence of H_2O_2 liberated in this process. The velocity of oxidation depends on the partial pressure of O_2, but oxidation can take place in a vac. or a N_2 atm. if a H-acceptor, such as benzoquinone or phloroglucinol, capable of forming a co-ordination compound with the ammine, is added. This constitutes another resemblance between complex metal ammines and dehydrases or oxidation-reduction enzymes. M. S. B.

Asymmetric oxidation. I. Y. Shibata and R. Tsuchida. **II.** Y. Shibata, Y. Tanaka, and S. Goda. **III. Inhibiting action of some asymmetric organic acids on asymmetric oxidation.** Y. Shibata and K. Sakai (Iwata Inst. Plant Biochem., Publ. 2, 159—166, 167—174, 190—200).—I. By observing the changes in optical rotation during the catalytic oxidation of *r*-3 : 4-dihydroxyphenylalanine (I) by *l*-$[Co\,en_2NH_3Cl]Br_2$ (II) (en=ethylenediamine) it is found that selective oxidation of *l*-(I) takes place.

(II). The catalytic oxidation of *d*-catechin (III) by *d*- and *l*-$(Co\,en_2NH_3Cl)Br_2$ has been studied both by changes in rotation and also by the amount of O_2 absorbed. Oxidation is more rapid by the *d*- than by the *l*-complex. Oxidation of (III) by *r*-complex follows a similar course to that by *l*-complex instead of lying between *d*- and *l*-. There is thus an analogy with the action of certain natural enzymes.

III. The action of optically active inhibiting agents on the oxidation of *d*-catechin by *d*- and *l*-(II) in buffered solutions depends on the sign of the rotation of the inhibitor. Inhibition by the combinations *d*-(II)+*d*-tartaric acid and *l*-(II)+*l*-tartaric acid is > by *d*-+*l*- or *l*-+*d*-combinations. *l*-Cysteine has a strong retarding influence on oxidation by both *d*-(II) and *l*-(II), but on *d*-(II) it is somewhat > on *l*-(II). The inhibiting action of *d*-bromocamphorsulphonic acid on catalysis by *l*-(II) is > on that by *d*-(II). M. S. B.

Oxidase-like action of certain complex metal salts. Metol. Y. Shibata and K. Yamasaki (Iwata Inst. Plant Biochem., Publ. 2, 1936, 180—189).—The autoxidation of p-$OH{\cdot}C_6H_4{\cdot}NHMe,H_2SO_4$ (I) is inhibited by complex Co salts, the inhibiting action being parallel with the oxidising action of these salts on polyphenols (cf. preceding abstracts). The Co salt forms an insol. ppt. with (I). On the other hand complex Cr salts, which are not oxidation catalysts, have no inhibiting action on the autoxidation of (I) and form no ppt. This supports the assumption (cf. first abstract of this group) that combination between complex and polyphenol is necessary before oxidation is accelerated. KCN and Cr complexes, which are poisons for the accelerating action, have a similarly inhibiting effect on the retarding action. NH_2OH, however, is an exception since, although a poison for catalytic oxidation, it accelerates the autoxidation of (I), but has practically no effect on the inhibiting action of Co complexes, the two effects being algebraically additive. M. S. B.

Catalytic reduction of complex metal salts. Y. Shibata and T. Yamabe (Iwata Inst. Plant Biochem., Publ. 2, 1936, 207—213).—The reduction of benzoquinone by H_2 is catalysed by complex Ni ammines. The reaction is also accompanied by evolution of O_2, probably due to the formation of H_2O_2 during the course of the reaction and subsequent splitting up by the Ni complex (cf. a previous abstract). In order to follow the rate of H_2 absorption O_2 must be absorbed by pyrogallol. For the same Ni ammine the rate of reaction varies with the p_H of the solution. M. S. B.

Mechanism of the catalytic exchange reaction between deuterium and water. A. Farkas (Trans. Faraday Soc., 1936, 32, 922—932).—The velocity of the reaction between HD and H_2O vapour on a Pt wire at 250—410° and 10—70 mm. is about 0·1 that of the ortho-para-H_2 conversion. The rate of the exchange reaction is independent of the H_2O pressure and increases nearly linearly with D_2 pressure, indicating that H_2O is strongly and H_2 weakly adsorbed.

E for the exchange reaction is 13·5 kg.-cal. The mechanism is discussed. L. J. J.

Kinetics of para–ortho-hydrogen conversion on charcoal. R. Burstein and P. Kashtanov (Trans. Faraday Soc., 1936, **32**, 823—828; cf. A., 1935, 940).—The rate of the *o*–*p*-hydrogen conversion on C has a positive temp. coeff. between 20° and 573° abs., whilst when the C is poisoned it is negative in the range 90—300°, and positive between 300° and 573° abs. The results indicate the existence of two kinds of active centres, one of which becomes inactive at 20° abs. F. L. U.

Catalytic preparation of sulphuryl chloride.—See B., 1936, 493.

Energetics of catalysis. VI. Kinetics of hydrogenation processes in liquid systems. E. B. Maxted and C. H. Moon (J.C.S., 1936, 635—637; cf. A., 1935, 1210).—The change in sign above 80—90° of the temp. coeff. of the reaction between crotonic acid and O_2 on a Pt surface is accompanied by a corresponding change in the kinetics of the reaction. This changes from zero order to approx. first order, in accord with the view that the change is due to a decrease in the concn. of acid adsorbed till it is insufficient to render the reaction independent of this concn. J. W. S.

Catalytic esterification of alcohols without the use of acids. P. J. Ivannikov and E. J. Gavrilova (J. Appl. Chem. Russ., 1936, **9**, 490—491).—EtOAc or $EtCO_2Pr$ is obtained in 50—60% yield by passing EtOH or PrOH over a Cu–U catalyst at 240°. R. T.

Influence of the carrier on poisoning of platinum catalysts by arsenic. I. E. Adadurov, A. N. Tzeitlin, and L. M. Orlova (J. Appl. Chem. Russ., 1936, **9**, 399—411).—The sensitivity to As_2O_3 poisoning of Pt catalysts is at a min. when the radius of the cation of the carrier is 0·78 A. (Mg, Sn, Zr), and the poisoned catalyst is most readily activated by heating in air or with CO–H_2. A study of the catalytic action of Pt on Be, Mg, Ca, Sr, Ba, Ti, Sn, Si, Zr, Th, Al, Fe, and Cr sulphates or oxides shows that the action of the carrier depends on the radius, but not on the chemical nature, of the cation. R. T.

Effects of various fluorides on thermal synthesis of calcium silicates. I. S. Nagai and M. Takahara (J. Soc. Chem. Ind. Japan, 1936, **39**, 130—132B; cf. A., 1935, 1085).—The efficiency of fluorides as catalysts in the synthesis of Ca silicates decreases in the order Na_3AlF_6, NaF, Na_2SiF_6, MgF_2, CaF_2, and $MgSiF_6$. Glass powder is slightly more efficient than felspar. R. S.

Catalytic oxidation by copper salts in presence of manganese salts. P. Thomas and (Mlle.) C. Kalman (Compt. rend., 1936, **202**, 1436—1437).—The oxidation of phenolphthalein or pyramidone by dil. H_2O_2 solution in presence of $Cu^{\cdot\cdot}$ is inhibited by $Mn^{\cdot\cdot}$. L. J. J.

Accelerators and retarders in the reduction of silver salts. G. Ollendorff and H. Andresen (Z. wiss. Phot., 1936, **35**, 119—123).—The speed of reduction of AgBr sols has been measured in the presence of various retarding agents, *e.g.*, gelatin, Tl salts, and accelerating agents, *e.g.*, Na_2S, $Na_2S_2O_3$, thiosinamine. Small amounts of KI accelerate reduction; with increasing amounts a min. speed is reached, and the rate then increases steadily with larger amounts. Lowering of p_H (omission of alkali from normal developer) also retards development. J. L.

Oxidation catalysis. II. Chromium oxide as catalyst. A. Kutzelnigg and W. Wagner. **III. General view.** A. Kutzelnigg (Monatsh., 1936, **67**, 231—240, 241—247; cf. A., 1930, 1133).—II. The activity of pure Cr_2O_3 [prepared by heating $Cr(OH)_3$ in H_2] in catalysing the oxidation of $K_4Fe(CN)_6$ by atm. O_2 rises with increase of drying temp. up to 450°, beyond which it decreases rapidly to zero. There is a secondary max. in the activity curve at 200°. The active Cr_2O_3 is olive-brown and amorphous, whilst the strongly heated inactive material is green and cryst. The particle size remains approx. const. When prepared in presence of O_2, the black oxide shows max. activity after heating at 300°. Finely divided Cr_2O_3 prepared by decomp. of Hg_2CrO_4 has the greatest activity and "glossy Cr_2O_3" the least of a no. of preps. tested, the products of decomp. of $(NH_4)_2CrO_4$, $Cr_2(C_2O_4)_3$, and $Cr(NO_3)_3$ being intermediate.

III. Besides Cr_2O_3, Fe_2O_3 and CuO show max. activity in catalysing the atm. oxidation of $K_4Fe(CN)_6$ when prepared at certain temp. This is associated with the elimination of adsorbed H_2O layers or salts from the powders. Whereas animal charcoal promotes the reduction of $K_3Fe(CN)_6$ in alkaline solution, only slight catalytic effect is found with MnO_2 and fuller's earth and none with NiO, Fe_2O_3, CuO, SiO_2 gel, PbO_2, ZnO, or Ag_2O. Oxides which catalyse the decomp. of $K_4Fe(CN)_6$ also promote the evolution of O_2 from $KClO_3$, $KMnO_4$, HgO, Ag_2O, and H_2O_2, the most active oxides being those of elements at the min. of the at. vol. curve. J. W. S.

Kinetics of hydrogenation of ethylene on skeletal contact catalysts. G. M. Schwab and H. Zorn (Z. physikal. Chem., 1936, B, **32**, 169—201).—Catalysts have been prepared by making alloys with the compositions NiSi, $NiSi_2$, and $NiAl_3$ and removing the Al with NaOH. The hydrogenation has been studied at 0—180° under total pressures, *p*, of 50—250 mm. During reaction the activity, *a*, of the catalyst falls, and may even decline at room temp., due to ageing. For a given catalyst $a \propto (m/d)^{2/3}$ (m=wt.), indicating that *a* is a linear function of the grain surface of the vol. near the surface. On fresh catalysts there are numerous active centres chiefly within the grains and accessible to the reactants only by diffusion, and the rate of the process as a whole is determined by the rate of diffusion. With fewer and less active centres the rate of hydrogenation is determined by the rate of a normal chemical reaction, requiring activation. The kinetics of the reaction on NiSi after ageing are of this type. Here reaction is of the first order in respect of *p*, but of fractional orders in respect of the partial pressures of H_2, p_1, and C_2H_4, p_2. The Langmuir–Hinshelwood theory is valid and the rate is given by $-dp/dt=kp_1p_2/(1+bp_1+cp_2)$, where *b* and *c* are adsorption coeffs. The true heat of activation is 18·7±1 kg.-cal., a val. which excludes the possibility of any "tunnel" reaction, and the calc. optimum temp. is 450—470° abs. On the more active $NiSi_2$ and $NiAl_2$ the kinetics are formally similar, but *b* and *c* are not adsorption coeffs. and the rate of diffusion is the governing factor; C_2H_4 now retards the reaction. *X*-Ray diagrams show that the active centres are probably located in the amorphous part of the catalysts. R. C.

Kinetics of the acetylation of cellulose fibres. V, VI. Influence of solvent and the concentration of sulphuric acid on the acetylation velocity in the fibre bundle and the ratio of the catalytic action of sulphuric and perchloric acids. I. Sakurada and M. Miyaguti (J. Soc. Chem. Ind. Japan, 1936, **39**, 91—94b; cf. A., 1935, 42).—The velocity of acetylation is given by $x=kt^m$ (x=mols. AcOH per 100 mols. $C_6H_{10}O_5$). *m* is approx. const. with increasing $[H_2SO_4]$ but *k* increases according to $k=pc^{1/q}$ where *p* and *q* are consts. The catalytic activity of $HClO_4$ is 10 times that of H_2SO_4 but the influence of different solvents is small. R. S.

Catalytic reduction of carbon monoxide to methane.—See B., 1936, 531.

[Catalytic] decomposition of methane and petroleum hydrocarbons with steam.—See B., 1936, 532.

[Catalytic] synthesis of ethyl acetate.—See B., 1936, 536.

Catalytic oxidation of benzene.—See B., 1936, 536.

Catalytic properties of rhenium. II.—See this vol., 820.

Catalytic action of colloidal ferric hydroxide at different degrees of dispersion. I. S. Teletov and A. V. T. Tjutjunkina (Ukrain. Chem. J., 1936, **11**, 1—3).—The velocity of catalytic decomp. of H_2O_2 by $Fe(OH)_3$ sols is a function of the degree of dispersion of the latter. R. T.

Decomposition of nitrous oxide on the surface of platinum. II. The effect of foreign gases. E. W. R. Steacie and J. W. McCubbin (Canad. J. Res., 1936, **14**, B, 84—89; cf. A., 1934, 1182).—Preliminary addition of N_2 diminishes the rate of decomp. of N_2O on sponge Pt by filling up the pores, but is without effect in the case of Pt gauze. The retarding effect of He, CO_2, and H_2O has also been studied and the adsorption isotherm of O_2 on Pt at 570° has been determined. O_2 formed by decomp. of N_2O gives the same isotherm, whilst adsorption of N_2O is small. It is concluded that O_2 does not retard the decomp. R. S.

Decomposition of hydrogen sulphide and water on molybdenum filaments. F. E. T. Kingman (Trans. Faraday Soc., 1936, **32**, 903—907).—H_2S decomposes at 400—685° and 0·1 mm. by a first-order reaction with *E* 25,000 g.-cal., giving H_2 and S. H_2O decomposes at 800—1200°, giving H_2 and Mo oxide, which retards the reaction below 1000°. Above 1000°, H atoms are formed and react with the Mo oxide. E=43,000 g.-cal. L. J. J.

Reaction mechanism. VII. Rate of catalytic hydrogenation of doubly linked carbon in chain molecules in solution. O. Schmidt (Z. physikal. Chem., 1936, **176**, 237—259; cf. A., 1933, 913).—The rate of hydrogenation at 20° of various aliphatic and aromatic hydrocarbons, alcohols, carboxylic acids, and esters having an ethenoid double linking in MeOH and other solvents with Ni, Pt, and Co as catalysts has been determined. Hydrogenation occurs in the micropores of the metal phase into which the org. mols. diffuse as far as their size allows. The rate of reaction is determined by the rate of this diffusion. The H_2 dissolves in the catalyst and is activated by being converted into protons. In general, the more substituents there are in the unsaturated mol. and the larger or less compact they are the slower is hydrogenation. Chain-branching retards diffusion and with it the reaction. With compounds of the type CH_2:CHR the time for half reaction, τ, falls only slightly as the chain length of R increases. In some cases the Ph group has a powerful retarding action. τ is particularly high for compounds of the type CR′R″:CHR. For an acid τ is > for its Me or Et ester, suggesting that CO_2H retards diffusion more than CO_2Me and CO_2Et. If the double linking is at the end of the chain the length and position of the substituents have little effect on the velocity. τ runs approx. parallel with the viscosity and heat of adsorption of the solvent and increases with its mol. wt. R. C.

Catalytic activity of palladium and overvoltage of hydrogen. C. A. Knorr and E. Schwartz (Z. physikal. Chem., 1936, **176**, 161—168).—Extension of a previous investigation (A., 1934, 258) shows that the val. of *b* in the logarithmic relation between overvoltage and c.d. falls with increasing catalytic activity of the Pd electrode. On pure active Pd *b* would probably approach the val. required by Tafel's theory of overvoltage, and it is inferred that here it is the slowness not of the discharge of the $H^{\cdot}$ ions but of the process $2H \rightarrow H_2$ which is responsible for overvoltage (cf. A., 1935, 705). R. C.

Catalytic action of Japanese acid clay. II. Promotive action of Japanese acid clay on [the] catalytic action of mercuric sulphate [in the] condensation of acetylene and acetic acid. T. Kuwata and O. Kato (J. Soc. Chem. Ind. Japan, 1936, **39**, 127—128b; cf. B., 1936, 138).—The efficiency of $HgSO_4$ in affecting condensation of C_2H_2 and AcOH is increased if it is pptd. on Japanese acid clay (I). Optimum conditions (79·5% yield) are: (I) (9·6 g.), leached with hot 18% HCl and dried at 150—200°, is added to HgO (2·88 g.) in AcOH (29 c.c.), to which 50% oleum (1·2 g.) is then added. Addition of (I) to a previously prepared catalyst or use of C has no effect. R. S. C.

Electrolysis of manganous salts. M. Geloso and (Mlle.) C. Rouillard (Compt. rend., 1936, **202**, 1418—1421).—Current–anode potential curves show two ascending branches, corresponding with deposition of $MnO_2,nMnO$, and evolution of O_2, respectively, and separated by a flat portion. Data are recorded for the variation of *n* with the conditions of electrolysis. Part of the current must be carried by OH'. L. J. J.

Electrochemical isolation of light metals from non-aqueous solutions. I. Alkali metal salts. M. A. Klotschko (J. Appl. Chem. Russ., 1936, **9**, 420—433).—The alkali halide is fused with $AlCl_3$ or $AlBr_3$, and a solution of the melt in $PhNO_2$ is electrolysed (Ag anode, Pt cathode, with electrode diaphragms). The yield of metal varies inversely with the c.d., max. vals. being obtained using 0·0002—0·001 amp. per sq. cm. The process consists of $MAlX_4 \rightleftharpoons M^{\cdot}+AlX_4'$; $AlX_4' \rightarrow AlX_3+X$ (M=Li, Na, K, Rb; X=Cl, Br). R. T.

Electrolysis of molten antimony sulphide.—See B., 1936, 552.

Electrolytic deposition of aluminium.—See B., 1936, 552.

Electro-deposition of nickel–cobalt alloys from solutions containing triethanolamine.—See B., 1936, 551.

Removal of sulphate from nickel hydroxide by electrodialysis.—See B., 1936, 555.

Electrolytic reduction of organic compounds. II. Catalytic hydrogenation of sorbic acid at prepared cathodes of nickel and platinum. E. Isaacs and C. L. Wilson (J.C.S., 1936, 574—576; cf. this vol., 454).—Electro-deposition of spongy Ni or Pt-black on the metals converts them into efficient reducing agents for sorbic acid (I). These cathodes differ from other metals in causing reduction of (I) mainly to Δ^{α}-hexenoic acid and hexoic acid, similar to the course of hydrogenation of (I) in EtOH solution with Adams' catalyst. J. W. S.

Electrolysis of magnesium methyl halides.—See this vol., 830.

Electrolytic oxidation of proline and γ-aminobutyric acid.—See this vol., 828.

Oxidation of sulphur dioxide in the high-voltage arc discharge. S. M. Golyand (J. Phys. Chem. U.S.S.R., 1934, **5**, 1471—1472).—A criticism of Kolodkina and Netschaeva's work (cf. A., 1935, 712). Ch. Abs. (*e*)

Oxidation of sulphur dioxide in the high-voltage arc discharge. N. Netschaeva and L. Kolodkina (J. Phys. Chem. U.S.S.R., 1934, **5**, 1473—1474; cf. preceding abstract).—A reply. Ch. Abs. (*e*)

Behaviour of gases under the influence of high-frequency discharge. Ammonia and hydrogen. B. S. Srikantan (J. Indian Chem. Soc., 1936, **13**, 79—85).—NH_3 is greatly adsorbed by the walls of highly evacuated glass tubes. When the walls are saturated with respect to NH_3, any further addition of NH_3 is immediately decomposed by the discharge into H_2 and N_2 which are adsorbed, leaving a residue of NH_3 in equilibrium with the adsorbed NH_3. Further discharge expels the N_2 from the walls. C. R. H.

Mechanism of the photochemical reaction between bromine and water. H. A. Pagel and W. W. Carlson (J. Physical Chem., 1936, **40**, 613—617).—The kinetics of the reaction have been investigated at 25°. The reaction appears to take place as follows: (1) $Br_2+H_2 \rightleftharpoons H^{\cdot}+Br'+HOBr$, (2) $HOBr+h\nu \rightarrow H^{\cdot}+Br'+\frac{1}{2}O_2$. E. S. H.

Oxidation of nitrites to nitrates in sunlight. N. R. Dhar and S. P. Tandon (J. Indian Chem. Soc., 1936, **13**, 180—184).—A study of the catalytic effect of ZnO, Fe_2O_3, TiO_2, and soil on the photo-oxidation of aq. solutions of $NaNO_2$ shows that in dil. solutions oxidation is complete but that in conc. solutions the equilibrium $2NaNO_2+O_2 \rightleftarrows 2NaNO_3$ is attained. It is suggested that the conversion of NH_4 salts into nitrates in soil may be due more to photochemical than to bacterial action. C. R. H.

Photochemical peroxide formation. I. Oxidation of methyl alcohol by molecular oxygen in ultra-violet light. R. Cantieni (Ber., 1936, **69**, [*B*], 1101—1106).—Aq. MeOH in presence of O_2 is oxidised with formation of peroxide in ultra-violet light of long and short λ. Peroxide formation from MeOH–O_2 also occurs in absence of H_2O, the presence of which retards its formation. The peroxide becomes less stable as its concn. increases. Its formation is about 120 times as rapid in unfiltered ultra-violet light as in that which has been filtered through glass. The hypothesis that H_2O_2 is produced from H_2O during the photochemical oxidation of MeOH is untenable and it is improbable that H_2O_2 arises by oxidation of H formed by photolysis. The production of OMe·OH is assumed which, in ultra-violet light, oxidises MeOH. CH_2O, as primary oxidation product, is present in traces when the concn. of peroxide is small. HCO_2H cannot be detected by reason of its ready oxidisability by peroxide in ultra-violet light. H. W.

Theory of densensitisation. K. Weber (Z. wiss. Phot., 1936, **35**, 124—128; cf. A., 1935, 1331).—The author's theory, that desensitisers act by oxidising the optical or chemical sensitisers present, is brought into agreement with the observations of Blau and Wambacher (this vol., 37) and Arens and Eggert (A., 1929, 277) by the assumption that the process is reversible in the absence of O_2. The reactions are treated mathematically, and are shown to be in agreement with various known data. J. L.

Action of light on catalytic oxidation by some metallic complex salts. Y. Shibata and S. Goda (Iwata Inst. Plant Biochem., Publ. 2, 1936, 175—179).—By the use of suitable light filters the influence of light of different λ between infra-red and 3300 A. on the oxidation of *d*-catechin in presence of *r*-$[Co\,en_2NH_3Cl]Br_2$ (I) (en=ethylenediamine) has been examined. Aq. (I) has absorption bands at λ 5000 and 3640 A., but light in this region is less active than the light of longer λ absorbed by H_2O. This confirms the theory previously put forward that oxidation takes place through the medium of activated H_2O. The following reaction scheme is proposed: $R+2H{\cdot}OH+0{\cdot}5O_2=R(OH)_2+H_2O$ and $R(OH)_2=RO+H_2O$. The mechanism of activation of H_2O by the complex salt is still obscure. M. S. B.

Photochemical activation of the oxidising action of complex metal salts. A. Watanabe

(Iwata Inst. Plant Biochem., Publ. 2, 1936, 129—158).—The catalytic oxidation of KI, pyrogallol, benzidine, p-$C_6H_4(NH_2)_2$, and Nadi reagent, and the catalytic decomp. of H_2O_2 by complex metal salts is accelerated by ultra-violet or visible light radiation. Photochemical reaction may take place even where there is no appreciable dark reaction. The infra-red radiation is active in the case of pyrogallol oxidation only. Preliminary irradiation of the separate constituents has no effect. The most active λ in the Hg arc is 366 mμ. Of the Co ammines containing NO_2 the most sensitive to light is $[Co(NH_3)_4(NO_2)_2]Cl$, and of the two stereoisomerides the *trans*- is more sensitive than the *cis*-form. The action is ascribed to the increased instability of the complex metal salt under the action of light. M. S. B.

Photochemical sensitisation in solutions. I. Sensitisation of an Eder solution with eosin. E. V. SCHPOLSKI and N. I. KOLESNIKOVA (J. Phys. Chem. U.S.S.R., 1934, 5, 1199—1209).—For light of λλ 5200 and 5460, 5760 A. there was a short induction period, after which the reaction proceeded linearly with time. Its rate was ∝ the light intensity. At concns. of 5×10^{-7} to 10^{-5} g. per c.c. the rate ∝ the concn. At concns. of 3×10^{-5} to 10^{-4} g. per c.c. the rate was const., and at higher concns. it decreased. The concn. thresholds for the decrease in sensitisation and the damping of fluorescence coincided. The rate ∝ $[HgCl_2]$ and was independent of $[C_2O_4'']$ for concns. $>$ 0·01 g. per c.c. The temp. coeff. was 2·6 at 5—15° and 1·9 at 15—25°. The dark reaction became appreciable at $>$ 30°. The quantum yield for λλ 5470, 5760 A., in presence of O_2, was 12·5. CH. ABS. (*e*)

Photochemical bleaching of chlorophyll.—See this vol., 867.

Photochemical reaction of chlorophyll with ferrous ions.—See this vol., 907.

Study of solid reactions by the emanation method. R. JAGITSCH (Monatsh., 1936, 68, 1—9).—The following changes have been observed, at the temp. indicated, on heating the respective materials containing Rd–Th as a source of Tn: α- → β-SiO_2 575°; β-SiO_2 → β-tridymite 870°; $SiO_2+CaCO_3 \rightarrow CaSiO_3$ about 900°; γ-Al_2O_3 → corundum 840—950°; $Al_2O_3+CoCO_3$, $Al_2O_3+Ca \rightarrow Co(Ca)Al_2O_4$ complete at about 900°; $Fe_2O_3+CaCO_3 \rightarrow CaFe_2O_4$ 550—600°. F. L. U.

Properties of sodium hexametaphosphate. R. T. THOMSON (Analyst, 1936, 61, 320—323).—A no. of insol. salts of Ca, Ba, etc. readily dissolve in aq. $Na_6P_6O_{18}$. Portland cement is attacked, most of the Ca and part of the SiO_2 being dissolved. E. C. S.

Crystallisation and loss of water from copper hydroxide. E. HAYEK (Monatsh., 1936, 67, 352—356).—Pure cryst. $Cu(OH)_2$ has been prepared by slow evaporation of NH_3 from a cold solution of CuO in conc. aq. NH_3 and shown to have a crystal structure identical with known forms. The relatively higher stability of this product, and of amorphous $Cu(OH)_2$ prepared by dilution of the CuO–NH_3 solution, compared with $Cu(OH)_2$ obtained by pptn. with alkali, indicates that adsorbed alkali is the cause of the dehydration process at lower temp. J. W. S.

Cuprous iodide. R. HUERRE (J. Pharm. Chim., 1936, [viii], 23, 594—605).—The formation of Cu_2I_2 from KI and $CuSO_4$ in H_2O is inhibited in dil. solution. HCl has no effect, but excess of KI and $Na_2S_2O_3$ favour the reaction. J. L. D.

Preparation of the complex salt, Cu_2HgI_4. P. G. POPOV (Ukrain. Chem. J., 1936, 11, 11—12).—8·3 g. of KI in 20 ml. of H_2O are added to 6·8 g. of $HgCl_2$ in 100 ml. of H_2O, the washed ppt. is dissolved in 20 ml. of 41·5% KI, and the solution is added to a solution of 5 g. of CuCl in 40 ml. of 50% HCl. The ppt. of Cu_2HgI_4 is washed with 50% HCl and H_2O, and dried at 100°. R. T.

Calcium metaphosphates. A. BOULLÉ (Compt. rend., 1936, 202, 1434—1435).—Data are recorded for the *X*-ray spectra of $Ca(PO_3)_2$ prepared by ignition of $Ca(H_2PO_4)_2$ at different temp. Ignition below 400° gives a new cryst. *form*, converted at higher temp. into a different modification, m.p. 1010±5°. Thermal analysis data are in agreement. L. J. J.

Hexamethylenetetramine compounds.—See this vol., 828.

Potentiometric study of complex thiosulphates. I. Strontium silver thiosulphate. R. PORTILLO and J. G. TÁNAGO (Z. anorg. Chem., 1936, 227, 124—128).—The *compounds* $[Ag_2(S_2O_3)_2]Sr,H_2O$ and $[Ag_2(S_2O_3)_3]Sr_2,6H_2O$ are described. Their formation is indicated by potentiometric titration of SrS_2O_3 with $AgNO_3$, both 0·1*N*. F. L. U.

Preparation of luminescent zinc orthosilicate. J. V. GOLBREICH and I. V. EGOROVA (J. Appl. Chem. Russ., 1936, 9, 446—450).—Max. cathodal luminescence is obtained when Zn_2SiO_4 containing 1% of Mn as $MnCl_2$ or $MnSO_4$ is heated for 30 min. at 1200°. R. T.

Ammoniates of simple salts. II. Ammoniates of zinc salts. G. SPACU and P. VOICHESCU (Z. anorg. Chem., 1936, 227, 129—144; cf. this vol., 573).—The existence of ammoniates of Zn salts of the following acids has been established by tensimetric methods (figures indicate no. of mols. of NH_3 per mol. of anhyd. salt): HCNS 8, 6, 4, 2; HCO_2H 10, 6, 4, 2; AcOH 8, 6, 4, 2, 1; $OH{\cdot}CH_2{\cdot}CO_2H$ 6, 4, 2; $NH_2{\cdot}CH_2{\cdot}CO_2H$ 5, 2, 1; $({\cdot}CH_2{\cdot}CO_2H)_2$ 6, 5, 3, 2, 1; $[{\cdot}CH(OH){\cdot}CO_2H]_2$ 2, 1; BzOH 8, 6, 4, 2; salicylic 8, 4, 2; *o*-aminobenzoic 10, 6, 4, 2; 5-sulphosalicylic 8, 4, 2. The stability of corresponding ammoniates increases with the strength of the acid. The influence of the mol. vol. of the metal and of the acid radical is discussed. F. L. U.

Preparation of crystalline aluminium hydroxide from chromate–aluminate solutions by precipitation with carbon dioxide. F. F. VOLF and A. E. MOROCHOVETZ (J. Appl. Chem. Russ., 1936, 9, 412—419).—Cryst. $Al(OH)_3$ is pptd. from Na aluminate–chromate solutions at 80—90° by saturation with CO_2; the product is readily filterable, and contains $\ngtr$ 0·03% of Cr_2O_3 after washing. R. T.

Activation of redwood and ash-free sugar charcoal in a current of air. J. W. MCBAIN and R. F. SESSIONS (J. Physical Chem., 1936, 40, 603—611).—The best conditions for activating C in air have been examined in relation to temp., duration of heating, and type of furnace. A peak of activation is observed at 350—450°, and a more pronounced peak at 920—960°. When kept for a long period, even in sealed tubes, a decrease in activity of 17—63% occurs. A higher degree of activity is attained by activating in air than by heating in N_2 or He.

E. S. H.

α–β Transition in zirconium in the presence of hydrogen. J. H. de Boer and J. D. Fast (Rec. trav. chim., 1936, **55**, 350—356).—The solubility of H_2 in Zr decreases with rise of temp. except through the transition point when H_2 is rapidly absorbed.

C. R. H.

Lead chlorocarbonate and its applications as intermediary in the preparation of alkali nitrates. G. Austerweil and B. Kourakine (Bull. Soc. chim., 1936, [v], **3**, 898—905).—The prep. of $PbCO_3,PbCl_2$ from $PbCl_2$ and $CaCO_3$ is described. When KNO_3 is prepared by interaction of $Pb(NO_3)_2$ and KCl, dissolved $PbCl_2$ can be removed by adding $PbCO_3$.

E. S. H.

Nature of active nitrogen. C. R. Dhodapkar (J. Univ. Bombay, 1935, **4**, Part II, 190→199).—The production and properties of active N_2 are described. The first positive system of N_2 ($B^3\Pi \rightarrow A^3\Sigma$) is due to the N_2 mol. The mechanism of the production and decomp. of active N_2 and the effects of impurities are discussed.

J. W. S.

Reaction of ammonia with phosphorus pentachloride. Amides of phosphorus and phospham. I, II. H. Moureu and P. Rocquet (Bull. Soc. chim., 1936, [v], **3**, 821—828, 829—841).—Published work is described (cf. A., 1935, 945, 1057).

E. S. H.

Basicity of phosphorous acid. I. J. Sperber and J. F. Bodmer (Ber., 1936, **69**, [*B*], 974—977).—Although only 2 H of H_3PO_3 can be replaced by metal it gives esters Et_3PO_3 and the view is expressed that it has exclusively the structure $P(OH)_3$. Attempts to prepare K_3PO_3 by fusion of K_3PO_4 with CuCN lead to a product with the reactions of PO_3'''.

H. W.

Disproportionation of sulphurous acid by hydrogen bromide–acetic acid to sulphuric acid and sulphur. F. Kröhnke and H. Timmler (Ber., 1936, **69**, [*B*], 1140—1142; cf. this vol., 592).—SO_2 and HBr in AcOH at room temp. slowly yield S and H_2SO_4: $3SO_2+2H_2O \rightarrow 2H_2SO_4+S$. The reaction appears complicated and the intermediate production of $SOBr_2$ and SBr_4 is assumed. S_2Br_2 can be isolated and this with H_2SO_4 are the products if the action takes place in an anhyd. medium or if dehydrating agents (Ac_2O, AcBr) are present. Reaction does not occur in the presence of > about 20% of H_2O.

H. W.

Sexavalent tellurium derivatives. I. Telluric acids. M. Patry (Bull. Soc. chim., 1936, [v], **3**, 845—860; cf. A., 1935, 1090).—Only two forms of telluric acid are recognised as definite compounds, viz., orthotelluric acid $Te(OH)_6$, and polymetatelluric acid $(H_2TeO_4)_{11\pm1}$. These forms exist in equilibrium in aq. solution; rise of temp. or concn. favours an increase in $(H_2TeO_4)_{11\pm1}$. By heating $Te(OH)_6$ in a sealed tube for a long time at 300°, β-*TeO_3* (*d* 6·22) is formed as a hard, grey, chemically inert mass.

E. S. H.

Preparation of chromic sulphide. S. M. Veller (Ukrain. Chem. J., 1936, **11**, 23—27).—The upper of the two layers formed when NH_4 hexahydrobenzoate is shaken with aq. Cr alum is $(C_6H_{11}\cdot CO_2)_3Cr$, a boiling benzine solution of which yields Cr_2S_3 with dry H_2S. Cr_2S_3 is also formed as an intermediate product from aq. $Cr_2(SO_4)_3$ as follows: $Cr_2(SO_4)_3+3(NH_4)_2S \rightarrow Cr_2S_3+3(NH_4)_2SO_4$; $Cr_2S_3+6H_2O \rightarrow 2Cr(OH)_3+3H_2S$.

R. T.

Action of molybdic acid on lævorotatory α-glycerophosphoric acid.—See this vol., 821.

Constitution of β-iron oxide monohydrate. I. M. Kolthoff and B. Moskovitz (J. Amer. Chem. Soc., 1936, **58**, 777—779).—When the β-oxide is shaken with dil. HCl in aq. NaCl, the [HCl] decreases continuously. The results show that the β-oxide has the structure β-FeO(OH), and is isomorphous with FeOCl, with which it forms mixed crystals.

E. S. H.

Ferrites. I. A. E. van Arkel, E. J. W. Verwey, and M. G. van Bruggen. **II.** E. J. W. Verwey, A. E. van Arkel, and M. G. van Bruggen (Rec. trav. chim., 1936, **55**, 331—339, 340—347).—I. *X*-Ray diagrams of mixtures of Fe_2O_3 and oxides of bivalent metals which have been heated to various high temp. indicate the formation of a ferrite phase which, at about 1300°, can dissolve considerable amounts of Fe_2O_3. The fusion points of several ferrites, most of which exhibit cubic spinel structure, were determined.

II. *X*-Ray investigations were extended to mixtures containing an excess of the bivalent metallic oxide. The influence of the oxide on the properties of the binary system is more marked than is the case when the Fe_2O_3 is in excess.

C. R. H.

Complex compounds of iridium. IV. (Sir) P. C. Ray and N. P. Ghosh (J. Indian Chem. Soc., 1936, **13**, 138—140).—$IrCl_3,3Et_2S$ and NH_3 at 100° form *$IrCl_3,2Et_2S,NH_3$*, m.p. 155°. At 130—140°, in addition to $IrCl_3,Et_2S,2NH_3$ and $(IrCl,5NH_3)Cl_2$ (A., 1934, 1209), a viscous liquid was obtained which, by the action of Ag_2SO_4, yielded *$(Ir,Et_2S,5NH_3)_2(SO_4)_3,2H_2O$*. Et_2S and $(NH_4)_2IrCl_6$ at 80° form *$IrCl_3,3Et_2S$* (+1$CHCl_3$), m.p. 171°.

C. R. H.

Chromatographic analysis and its application. G. Hesse (Angew. Chem., 1936, **49**, 315—320).—A review of the technique and applications of chromatographic analysis, and of the relation of degree of adsorption to structure of adsorbate.

J. S. A.

Chelidonine: a fluorescent principle. M. Déribéré (Ann. Chim. Analyt., 1936, [iii], **18**, 119—120).—Practical applications of the brilliant fluorescence of chelidonine are discussed.

J. S. A.

Neville and Winther's acid as fluorescent indicator. M. Déribéré (Ann. Chim. Analyt., 1936, [iii], **18**, 120).—The acid shows a sharp change from no fluorescence to intense blue at p_H 6—6·5.

J. S. A.

Determination of deuterium content of hydrogen mixtures by Farkas' micro-thermal conductivity method. K. Wirtz (Z. physikal. Chem., 1936, B, 32, 334—340).—The difficulties in the method are discussed and ways of overcoming them described. An accuracy of ±0·1% is attainable. R. C.

Drying of substances decomposing when heated. V. F. Malachov (J. Appl. Chem. Russ., 1936, 9, 775—777).—The substance (NH_4NO_3) is dried until the loss in wt. in unit time becomes const., and the part of the drying curve representing this period is produced back to zero time, giving the original dry wt. R. T.

Determination of dry substance content.—See B., 1936, 527.

Drop reaction for hydrogen peroxide. L. Kulberg and L. Matveev (J. Appl. Chem. Russ., 1936, 9, 754—755).—A drop each of 1% *o*-tolidine in EtOH, acetate buffer at p_H 4, 1% aq. $FeSO_4$, and of the solution under examination are placed on filter-paper; a blue coloration develops in presence of $2{\cdot}5\times10^{-8}$ g. of H_2O_2. R. T.

Phenosafranine, tartrazine, and rose-Bengal as adsorption indicators. A. J. Berry (Analyst, 1936, 61, 315—319; cf. A., 1932, 1009).—A method for determining the constituents of mixtures containing CN′, I′, and Cl′ is described. Since AgBr is intermediate between AgCl and AgI in solubility and adsorption capacity for dyes, Br′ cannot be determined by this method in presence of other halides. The use of adsorption indicators in titrating $Ag^{\cdot}$ in acid solution with KBr and in systems such as Tl^{I}–Tl^{III} halides is described. The particular conditions for which the three indicators are best adapted are discussed. E. C. S.

Determination of hypochlorite and chlorate.—See B., 1936, 541.

Determination of bromine.—See this vol., 914.

Detection and determination of hydrobromic acid in hydrochloric acid. L. Chelle (Ann. Falsif., 1936, 29, 229—231).—The presence of Br (120 mg. per litre; determined by the method of Denigès and Chelle, B., 1913, 141) in samples of "pure" HCl is noted. E. H. S.

Acidimetric determination of iodine. R. I. Alexeev (J. Appl. Chem. Russ., 1936, 9, 547—551).—10 ml. of 13% $AgNO_3$ are shaken with 25 ml. of approx. 0·1*N*-I in KI, the ppt. is collected and washed, and the filtrate+washings are titrated with 0·1*N*-NaOH. The [I] is calc. from $61+3H_2O+6AgNO_3 \rightarrow 5AgI+AgIO_3+6HNO_3$. R. T.

Determination of iodine in basic slag and mineral fertiliser.—See B., 1936, 541.

Determination of small quantities of fluorine in dicalcium phosphate. S. E. Harris and W. G. Christiansen (J. Amer. Pharm. Assoc., 1936, 25, 306—310).—F is isolated as H_2SiF_6 by distillation with $HClO_4$ and determined colorimetrically by the fading effect on Zr alizarin lake. F. O. H.

Determination of fluorine. I. A. A. Vasiliev (J. Appl. Chem. Russ., 1936, 9, 747—750).—50 ml. of H_2O, 2 ml. of 2*N*-HNO_3, 10 drops of AcOH, and 25 ml. of 2·84% KBr are added to 50 ml. of neutral aq. NaF (containing 0·1 g. of NaF), the mixture is heated to 40°, and 25 ml. of a solution of 5·6% $Pb(OAc)_2,3H_2O$ in 1% AcOH are added. The ppt. of PbFBr is collected after 12—18 hr., washed successively with H_2O, aq. $PbBr_2$, and H_2O, and dissolved in 100 ml. of H_2O containing 5 ml. of HNO_3. 50 ml. of 0·1*N*-$AgNO_3$ are added, the solution is heated at 100° for 30 min., filtered, and the ppt. of AgBr is washed. Excess of $AgNO_3$ is determined in the filtrate+washings by titration with 0·1*N*-NH_4CNS. Alternatively, the ppt. of PbFBr is dried at 105° and weighed. R. T.

Instrument for automatic quantitative indication of hydrogen sulphide in the atmosphere. R. Kraus (Chem. Fabr., 1936, 9, 241—242).—A continuous record of H_2S in the air is made by traversing $Pb(OAc)_2$ paper past a slit. The tint may be calibrated by exposure to the gas liberated by acid from measured amounts of aq. Na_2S. J. S. A.

Determination of small amounts of hydrogen sulphide in air. I. S. Schereschevskaja (J. Appl. Chem. Russ., 1936, 9, 572—575).—H_2S is absorbed by 1% aq. $AgNO_3$, the ppt. of Ag_2S is treated with KCN, and the coloration given with Na plumbite by the K_2S formed is compared with those given by a series of standards prepared analogously from Ag_2S obtained by adding 0·1*N*-$Na_2S_2O_3$ to aq. $AgNO_3$. The method serves for the determination of $\not<$ 0·01 mg. of H_2S. R. T.

Gravimetric determination of selenates. (Mme.) Ripan-Tilici (Bull. Soc. chim., 1936, [v], 3, 881).—A claim for priority (cf. Spacu, this vol., 442). E. S. H.

Gravimetric determination of selenates. P. Spacu (Bull. Soc. chim., 1936, [v], 3, 881).—A reply (cf. preceding abstract). E. S. H.

Determination of selenium in steel.—See B., 1936, 548.

[Determination of nitrogen by the] Kjeldahl method. Le Tourneur-Hugon and Chambionnat (Ann. Falsif., 1936, 29, 227—229).—Digestion is completed in about 30 min. if $HClO_4$ is gradually added to the boiling liquid when the material has dissolved, *i.e.*, after about 12 min. using Gunning's technique. E. H. S.

Alkalimetry in presence of nitrite. A. S. Vetrov (J. Appl. Chem. Russ., 1936, 9, 772—774).—2 g.-mol. of H_2O_2 per g.-mol. of HNO_2 present are added to 20 ml. of the alkaline solution at 50—60°, 50 ml. of 0·1*N*-H_2SO_4 are added, followed by 3 drops of 0·2% Me-red, and the solution is titrated with 0·1*N*-NaOH. R. T.

Photometric study of the diphenylamine reaction for determining small amounts of nitrates in water. A. V. Trofimov (J. Appl. Chem. Russ., 1936, 9, 756—771).—Max. sensitivity is obtained when the final solution contains 73 g. of H_2SO_4 per 100 ml., and 100 mols. of $NHPh_2$ per mol. of HNO_3; under these conditions 5 mg. of HNO_3 per cu. m. of H_2O may be determined. The most satisfactory reagent for low [HNO_3] is one containing 10 mg. of $NHPh_2$ per litre of 89% H_2SO_4, taking 5 ml. of reagent to

2 ml. of H_2O. High or low results are obtained, according to whether the Cl′ content of the standard is > or < that of the H_2O. SO_4'' ($\not>$ 10% of $MgSO_4$ or Na_2SO_4), HCO_3' ($\not>$ 0·1%), and $HgCl_2$ ($\not>$ 0·3%) do not interfere. The rate of development of colour increases with rising temp., and that of fading still more so; using the above reagent, however, the coloration remains const. at 25° for $\not<$ 20 hr. R. T.

Distillation and separation of arsenic, antimony, and tin. J. A. Scherrer (J. Res. Nat. Bur. Stand., 1936, 16, 253—259).—The sulphates are distilled in an all-glass apparatus with HCl (*d* 1·18), in a stream of CO_2. $AsCl_3$ distils up to 112°; H_3PO_4 is then added and $SbCl_3$ distilled at 155—165°; Sn is distilled at 140° from a 75% HCl (*d* 1·18)–25% HBr (40%) mixture. Ge, Re, and Mo, but not Bi, interfere. L. J. J.

Salts of silicomolybdic acid with organic bases: gravimetric determination of small amounts of silica as pyramidone silicomolybdate. E. J. King and J. L. Watson (Mikrochem., 1936, 20, 49—56).—In dil. acid solution SiO_2 (1 mol.) combines with MoO_3 (12 mols.) to form a stable complex which yields insol. compounds (silicomolybdates) with org. bases (*e.g.*, coniine, C_5H_5N, and pyramidone). Since 1 mol. of complex combines with 3 mols. of pyramidone, conversion of SiO_2 into the heavy pyramidone silicomolybdate yields a weighable ppt. from a very small amount of SiO_2. J. W. S.

Determination of silica by means of 8-hydroxyquinoline. M. I. Volinetz (Ukrain. Chem. J., 1936, 11, 18—22).—0·25 g. of the substance is melted with 5 g. of NaOH, the melt is extracted with 200 ml. of H_2O, 30 ml. of conc. HCl are added, the solution is boiled, cooled, and made up to 1 litre. 20 ml. of 20% $(NH_4)_2MoO_4$ are added to 100 ml. of the solution, excess of 50% HCl is added, and an amount of 8-hydroxyquinoline (I) given by $0·024153P+0·21$ g., where *P* is the expected SiO_2 content of 1 g. of substance. The mixture is heated at 60—70°, cooled, made up to a known vol., filtered, and excess of (I) in 100 ml. of filtrate is determined bromometrically. Alternatively, the ppt. of $SiO_2,12MoO_3,4C_7H_6N\cdot OH$ is collected, washed, and weighed. R. T.

Spectrographic method of measuring carbon dioxide concentration. E. D. McAlister (Physical Rev., 1936, [ii], 49, 704).—An accurate and rapid method, independent of humidity and of the presence of other gases, and having very small temp. and pressure corrections, is described. It depends on the high opacity of CO_2 to radiation in the region of one of its fundamental absorption bands (4·2—4·3 μ); this, isolated from a Nernst filament, falls on a vac. thermocouple after passing through a known optical path length of air containing CO_2. The method is sensitive to 0·0001%. N. M. B.

Determination of carbon dioxide in gas mixtures.—See B., 1936, 541.

Colorimetric determination of atmospheric carbon dioxide.—See B., 1936, 493.

Micro-determination of potassium. P. Wenger, C. Cimerman, and C. J. Rzymowska (Mikrochem., 1926, 20, 1—28).—Emich's method (pptn. with H_2PtCl_6), with modified washing treatment, enables about 0·5 mg. of K to be determined in presence of 5 mg. Na. A micro-method has also been developed involving conversion into $KClO_4$ before pptn. with H_2PtCl_6. The use of Pregl tubes for filtration was unsatisfactory. The K_2PtCl_6 ppt. can be treated with KI and titrated with $Na_2S_2O_3$, this method being advantageous for determination of K in biological media. Examples relate to blood sera and cerebrospinal fluid, which are preferably mineralised with a mixture of conc. HNO_3 (5 vols.) and $HClO_4$ (*d* 1·67, 2 vols.). Ignition of the media causes loss of K. Micro-hot plates, filters, and water-baths are described. J. W. S.

Micro-determination of potassium. C. Cimerman and C. J. Rzymowska (Mikrochem., 1936, 20, 129—143).—A review.

Gravimetric determination of the titre of silver nitrate solutions. E. N. Taran (J. Appl. Chem. Russ., 1936, 9, 520—525).—2 ml. of 15% aq. NH_3 and 1 ml. of 40% aq. CH_2O are added to 50 ml. of aq. $AgNO_3$, the solution is heated at 100° for 20 min., and the pptd. Ag is collected, ignited, and weighed. R. T.

Micro-detection of beryllium with alkannin and naphthazarin. J. V. Dubský and E. Krametz (Mikrochem., 1936, 20, 57—58).—Addition of 2 drops of quinalizarin reagent [30 drops of 0·05% solution of quinalizarin in EtOH with 5 drops of 10% $(CH_2\cdot NH_2)_2$] to 3 drops of test solution yields a blue colour with $> 0·135\times10^{-6}$ g. Be. Similar addition of 1 drop of naphthazarin or alkannin reagent [30 drops of 0·03% naphthazarin solution in EtOH or 0·05% alkannin solution, with 5 drops of 10% $(CH_2\cdot NH_2)_2$] gives reddish-violet colours with $> 1·3\times10^{-6}$ g. Be. Use of NH_3 or NaOH in place of $(CH_2\cdot NH_2)_2$ reduces the sensitivity to 2×10^{-6} g. J. W. S.

Coloured and dyed crystalline precipitates. L. Rosenthaler (Mikrochem., 1936, 20, 85—90).—The ppts. obtained on adding a 1% solution of Orange II in 0·1*N*-HCl to solutions of various alkaloids, and on adding an NH_3 solution of rhodamine GH to NH_3 solutions of various derivatives of barbituric acid, are described. In NH_3 solution Orange II also gives ppts. with $Ca^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Th^{\cdot\cdot\cdot\cdot}$, $Co^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, and $Cd^{\cdot\cdot}$, and in 0·1*N*-HCl with alkaline-earth metals and many heavy metals. J. W. S.

Microchemical detection of magnesium by means of 8-hydroxyquinoline. M. V. Gaptschenko and O. G. Scheintzis (J. Appl. Chem. Russ., 1936, 9, 541—543).—A drop of aq. NH_3 is added to a drop of 10% Na citrate in 2*N*-NaOH, and a drop of solution is added, followed by a drop of 5% hydroxyquinoline in EtOH; characteristic crystals of the Mg salt are obtained when the solution contains $\not<$ 3·76 mg. of Mg per 100 ml. R. T.

Detection of cupric ion. B. M. Bogoslovski and V. S. Krasnova (J. Appl. Chem. Russ., 1936, 9, 751—753).—1—2 ml. of 0·5% p-$NH_2\cdot C_6H_4\cdot OH$ (I) and 25—30 ml. of saturated aq. NaCl are added to 200 ml. of solution; a violet coloration appears in presence of $\nless$ 0·6 mg. of Cu^{II}. The method also serves for detection of (I). R. T.

Nephelometric determination of copper with salicylaldoxime in lead-free substances. F. Alten, B. Wandrowsky, and E. Knippenberg (Mikrochem., 1936, **20**, 77—84).—The test and standard solutions, neutralised with NH_3, are treated with 3 c.c. of 30% AcOH, 1 c.c. of 20% K citrate, 2 c.c. of saturated aq. KH_2PO_4, and 0·5 c.c. of saturated aq. NaOAc, stirred, and brought into temp. equilibrium in a water-bath. 1 c.c. of 1% salicylaldoxime solution is added, and then after 1·5—2·5 hr. 1 c.c. of AcOH. The relative opacities are observed after a further 30 min. J. W. S.

Microgravimetric determination of small amounts of mercury vapour in air. V. A. Piankov (J. Appl. Chem. Russ., 1936, **9**, 580—582).—The air is passed over crystals of I, the HgI condensing in a cooled glass spiral is washed with Et_2O, the extract is conc. to 1—2 ml., filtered through asbestos, the filtrate+washings are evaporated to dryness at 40°, and the residue of HgI is weighed. Trustworthy results are obtained for concns. of $\nless$ 0·385 mg. of Hg per cu. m. of air (0·077 mg. of Hg). R. T.

Separation of aluminium from manganese, nickel, cobalt, and zinc. T. Kôzu (J. Chem. Soc. Japan, 1935, **56**, 683—688; cf. A., 1935, 1338).—Al is pptd. quantitatively from sulphate solution at room temp. by adding saturated aq. NH_2Ph. Zn interferes, but K, Mn, Ni, and Co do not. Ch. Abs. (*e*)

Solution of the manganese problem in analysis of silicate rocks. O. Hackl (Z. anal. Chem., 1936, **105**, 81—95).—The mineral is fused with Na_2CO_3, and SiO_2 is removed by a twofold separation. Fe, Al, Mn, Ti, etc. are pptd. by aq. $NH_3+H_2O_2$. The ppt. is partly dissolved in cold 40—50% HNO_3, and repptd. with $NH_3+H_2O_2$. The solution is conc., and Al+Fe completely separated by addition of NH_3. The united oxide ppt. is fused with $KNaS_2O_7$, and the melt is dissolved in 10% H_2SO_4; dissolved Pt is removed by H_2S. To the solution, 2—5% aq. Ag_2SO_4 is added, and then solid $K_2S_2O_8$. The solution is warmed at 75—80° for $\ngtr$ 5 min., cooled rapidly, and colorimetered for Mn. H_2O_2 is then added, and Ti so determined colorimetrically. Finally H_2O_2 is destroyed by heating at 100°, $Fe^{\cdots}$ is reduced by means of H_2S, and Fe is determined volumetrically. For the accurate colorimetry of Mn, solutions must be matched by dilution at equal thicknesses. J. S. A.

Formation of hydrogen peroxide in the silver reductor: micro-analytical method for iron. C. F. Fryling and F. V. Tooley (J. Amer. Chem. Soc., 1936, **58**, 826—831).—Determination of small amounts of Fe by reduction with Ag followed by titration with $Ce(SO_4)_2$ is complicated by the formation of H_2O_2. The procedure is applicable to the determination of about 1·5 mg. of Fe when the reduction is performed in an atm. of H_2 and a correction is applied for the indicator. E. S. H.

Oxidation–reduction indicators. I. *N*-Phenylanthranilic acid. A. Kirssanov and V. Tscherkassov (Bull. Soc. chim., 1936, [v], **3**, 817—821).—The use of *N*-phenylanthranilic acid in the titration of Fe, V, and Cr solutions is described. The oxidation–reduction potential is 1·08 volt. E. S. H.

Detection of cobalt in presence of other cations. A. T. Tscherni (Ukrain. Chem. J., 1936, **11**, 13—14).—The solution is made acid with HCl, NH_4CNS is added, and the mixture is shaken with EtOH–Et_2O; the upper layer is coloured blue in presence of Co. If Fe is present NH_4F is added to discharge the red coloration obtained. R. T.

Determination of chromium and chromates in waste water.—See B., 1936, 574.

Determination of chromium in chromite.—See B., 1936, 541.

Determination of tin in alloys with antimony and lead (antimony less than 2%). H. F. Hourigan (Analyst., 1936, **61**, 328—333).—Sn and Pb in the alloy are dissolved in conc. aq. HCl in absence of O_2, Sb is removed by filtration, and $SnCl_2$ determined by titration with KIO_3. In presence of Sb^{III} in solution, the latter titration gives erratic results. E. C. S.

Colorimetric determination of titanium in presence of bromine compounds. H. A. Liebhafsky (Z. anal. Chem., 1936, **105**, 113—114; cf. this vol., 45).—Contrary to the statement of Lutschinski and Lichatscheva, Br is best removed as AgBr by treating the acid solution with an excess of H_2O_2, followed by $AgNO_3$. J. S. A.

Colorimetric detection of titanium and vanadium in steel.—See B., 1936, 548.

Drop reaction for zirconium. N. A. Tananaev and A. V. Tananaeva (J. Appl. Chem. Russ., 1936, **9**, 526—531).—Zr is detected in presence of other elements (except Si) by pptn. as phosphate from solutions containing 25—30% of H_2SO_4 or 20—22% of HCl or HNO_3. Directions are given for the detection and approx. determination of Zr in minerals, involving fusion with NaOH, elimination of SiO_2 from the extract of the melt, pptn. of Zr as above, and ignition of the washed ppt., which is weighed as pyrophosphate. R. T.

Determination of small amounts of germanium. N. S. Poluektov (Z. anal. Chem., 1936, **105**, 23—26).—Na_2GeO_3 solutions are acidified, freed from CO_2, and neutralised with NaOH (phenolphthalein+*p*-nitrophenol). Mannitol (I) is added, and the monobasic (I)–GeO_2 complex acid thereby formed is titrated with 0·1*N*-NaOH. $<$ 1 mg. of Ge is determined colorimetrically as Mo-blue by the reduction of germanomolybdic acid by $FeSO_4$. Ge is first separated as GeS_2, which is dissolved in $NaOH+H_2O_2$, and treated with aq. $(NH_4)_2MoO_4$ containing $FeSO_4$ in presence of NaOAc. J. S. A.

Detection of vanadium. E. I. Kretsch (Ukrain. Chem. J., 1936, **11**, 28—31).—The substance, containing $\nless$ 0·2 mg. of V_2O_5, is mixed with an equal wt. of C, Cl_2 is passed over the mixture at 300—400°, and the issuing gases are passed through glass wool moistened with conc. H_2SO_4; V is indicated by a yellow to orange coloration. R. T.

Quantitative spectral analysis, detection [and determination] of vanadium in steel, and investigation of minerals from the Dreiser Weiher (Eifel) and the Finkenberg, near Beuel-on-Rhine. W. Siemeister (Z. anal. Chem., 1936, **105**, 1—22).—(*a*) Sensitive lines of V in the condensed spark discharge in presence of Fe are given. In presence of $\not>$ 1% of C, Mn, P, or Si, the photometric method of Hartley and de Gramont may be employed for determining V. In high alloy steels, owing to abnormal intensity relationships, the homologous line-pair method of Gerlach and Schweitzer is applicable. Where inhomogeneities (inclusions or segregations) occur, the material is first dissolved chemically. (*b*) Olivine, augite, and accompanying minerals from olivine bombs have been analysed spectrographically for Ni, Co, Mn, and Cr. SiO_2 and Fe must first be removed chemically, Fe being extracted quantitatively by Et_2O from the HCl solution of the mineral. Ni, Mn, Co, and Cr are pptd. with $(NH_4)_2S$, and the arc spectrum of the ppt., on C electrodes, is matched against samples of known composition. J. S. A.

Microchemical detection of bismuth by means of quinoline thiocyanate. M. V. Gaptschenko and O. G. Scheintzis (J. Appl. Chem. Russ., 1936, **9**, 544—546).—A drop of solution (made acid with HNO_3) is added to a drop of reagent (1 g. of NH_4CNS in 100 ml. of saturated aq. quinoline) on a slide; characteristic yellow crystals, of the composition $C_9H_7N,HCNS,Bi(CNS)_3$, are obtained in presence of $\not< 0{\cdot}3\times10^{-6}$ g. of Bi. Zn, Sn^{II}, Sb^{III}, Hg^{I}, Ag, and Cu interfere. R. T.

Micro-determination of m.p. R. C. Ray and V. Dayal (Trans. Faraday Soc., 1936, **32**, 741—743).—The angle of a V-shaped electrically heated Pt wire is brought in contact with a minute quantity of the powdered solid on a mica platform, and melting is observed microscopically. The method is rapid and fairly accurate. F. L. U.

Laboratory thermoregulator. J. S. Buck (J. Chem. Educ., 1936, **13**, 131). L. S. T.

Thermocouples for psychrometric purposes. R. W. Powell (Proc. Physical Soc., 1936, **48**, 406—414).—Factors affecting the wet-bulb depression are investigated. N. M. B.

Installation at the Bellevue Electromagnetic Laboratory of apparatus for helium liquefaction and production of temperatures below 1° abs., by the magnetic method. N. Kürti, P. Lainé, B. V. Rollin, and F. Simon (Compt. rend., 1936, **202**, 1421—1423).—The apparatus is described. Certain paramagnetic salts become ferromagnetic at very low temp. L. J. J.

Focussing effect of double-crystal spectrometer. R. C. Spencer (Physical Rev., 1936, [ii], **49**, 704; cf. A., 1931, 1205; Barnes, A., 1933, 993).—An extension of the discussion by Parratt (cf. this vol., 181). N. M. B.

Heterochromatic photometry of the ultraviolet region. E. J. Bowen (Proc. Roy. Soc., 1936, **A**, **154**, 349—353).—A quartz cell containing æsculin solution, placed before a K photo-electric cell, can be used as a relative quantum counter for λ 3665—2500 A. with a sensitivity much > that of a thermopile–galvanometer combination. L. L. B.

Technique of the far infra-red investigations. N. R. Tawde, Y. G. Naik, and D. D. Desai (J. Univ. Bombay, 1935, **4**, Part II, 181—189).—The apparatus is described. J. W. S.

X-Ray tubes with rotating anti-cathode. V. Linnitzki and V. Gorski (Tech. Phys. U.S.S.R., 1936, **3**, 220—222).—The rotating anti-cathode simultaneously functions as a mol. Gaede pump, thus avoiding the presence of Hg vapour and giving compactness. R. S. B.

Starting the Daniels–Heidt capillary mercury-arc lamp. L. D. Wilson (J. Amer. Chem. Soc., 1936, **58**, 856—857).—A magnetic device is described. E. S. H.

Stand for spark gap and interrupted arc. A. Schleicher and N. Kaiser (Z. anal. Chem., 1936, **105**, 114—115).—Arc or spark gap and interrupter are mounted as a single rigid unit. J. S. A.

Voltage sources and amplifiers for Geiger counters. N. S. Gingrich (Rev. Sci. Instr., 1936, [ii], **7**, 207—210).—A description is given of a modified pentode stabiliser in which a Ne lamp replaces the usual battery for maintaining a const. grid bias, a simpler stabiliser in which a bank of Ne lamps supplies the stabilised voltage directly, and a new amplifier using two standard radio tubes and a small Ne lamp. A brief report is made of the use of a "Strobotron" in counter circuits. N. M. B.

Thin windows for photo-electric cells and counters. G. P. Harnwell (Rev. Sci. Instr., 1936, [ii], **7**, 216).—A method of blowing from glass tubing a very thin window of uniform thickness and capable of withstanding large pressure differences is described. N. M. B.

Determination of coefficient of magnetisation of solids. C. Courty (Bull. Soc. chim., 1936, [v], **3**, 929—933).—Good results are obtained, using the magnetic balance, when the solid is immersed in a non-solvent liquid. E. S. H.

Charts for determining p_H values when using quinhydrone and hydrogen electrodes and saturated calomel cell. G. N. Pulley (Food Res., 1936, **1**, 141—144).—Corrections for temp. between 16° and 32° are recorded graphically. E. C. S.

Apparatus for the micro-electrolysis of large volumes of solution. B. L. Clarke and H. W. Hermance (Mikrochem., 1936, **20**, 126—128; cf. A., 1932, 492).—Improvements in the previous apparatus are described. J. W. S.

Properties of the immersion objective when used with rapid electrons. R. Behne (Ann. Physik, 1936, [v], **26**, 372—384). A. J. M.

Blocking layer in a selenium valve photo-electric cell. S. Freivert (Tech. Phys. U.S.S.R., 1936, **3**, 266—267).—The sensitivity of Se valve photo-cells decreases when the cell is placed in a vac., and reaches zero in 3—4 hr. The sensitivity is not regained by keeping in air. The resistance of the cell is reduced and the rectifying properties are lost, the Se changing from grey to bluish. A shellac coating almost stops the decay in a vac. and it is suggested that the blocking layer is one either of gas or of SeO_2, which is volatile. R. S. B.

Automatic potentiometer for thermal analysis. R. J. M. Payne (J. Sci. Instr., 1936, **13**, 158—161).—Improvements on an apparatus previously described (this vol., 45) are recorded. C. W. G.

Flask with graduated neck for the rapid adjustment of titrated solutions. J. Bouillot (J. Pharm. Chim., 1936, [viii], **23**, 557—558).—A 925-c.c. flask with narrow neck graduated up to 1200 c.c. is described. E. W. W.

Micro-volumetric analysis with weight burettes. L. Szebellédy and O. Clauder (Z. anal. Chem., 1936, **105**, 26—31).—The use of hypodermic syringes as wt. burettes for precision microtitrations is described. J. S. A.

Accurate automatic mercury pipette. P. H. Bigg (J. Sci. Instr., 1936, **13**, 156—157).—The flow of Hg ceases automatically after filling and after delivery of 0·3125±0·003 ml. C. W. G.

Apparatus with two thermionic vacuum tubes for automatic titration. T. Tashiro and Y. Kato (J. Chem. Soc. Japan, 1935, **56**, 757—766).
Ch. Abs. (*e*)

Pregl's absorption apparatus for the microdetermination of carbon and hydrogen. Influence of the nature of the capillary on the constancy of the increase in weight. H. Lieb and A. Soltys (Mikrochem., 1936, **20**, 59—64).—The capillary constriction in Pregl's absorption apparatus must have a length of 4—6 mm. and cross-section of 0·2—0·3 mm. or inaccurate results are obtained. J. W. S.

Atomising apparatus. B. Claus (Z. tech. Phys., 1935, **16**, 202—205; Chem. Zentr., 1935, ii, 1411).—The apparatus operates by the attuned piezoelectric vibrations of two SiO_2 plates, and is applicable to the dispersion of substances deposited electrolytically. J. S. A.

Absorption tube. K. Wagenmann (Chem.-Ztg., 1936, **60**, 469).—A compact $CaCl_2$ or soda-lime tube, with externally ground tap-stopper, is described. J. S. A.

Fundamentals of vacuum technique for chemical laboratories. G. Mönch (Chem.-Ztg., 1936, **60**, 465—468).—A review of general technique and apparatus. J. S. A.

Small multiple still. F. R. Pratt (Rev. Sci. Instr., 1936, [ii], **7**, 211—213).—The construction of, and performance data for, a simplified, economical, automatic still are given. N. M. B.

Apparatus with ground-glass joints. H. Lee (Analyst, 1936, **61**, 334).—The apparatus figured is suitable for the determination of NH_3 in H_2O and for the oxidation of org. matter with HNO_3–H_2SO_4. E. C. S.

Measurement of streaming of structure-viscous liquids. W. Philippoff (Kolloid-Z., 1936, **75**, 155—161).—Experiments with cellulose trinitrate in BuOAc show that viscosimeters of the capillary or Couette type give concordant results. E. S. H.

Manometer of small volume. R. A. Hull (J. Sci. Instr., 1936, **13**, 165—166).—Tetralin is a satisfactory liquid for use in simple U-tube manometers. C. W. G.

Vacuum joints in metal apparatus. R. M. Archer (J. Sci. Instr., 1936, **13**, 161—165).—Instructions are given for making metal–metal tube, metal–glass tube, metal–metal equatorial, and metal tube–spun nipple joints. C. W. G.

[Ultrafiltration.] H. J. C. Tendeloo (Chem. Weekblad, 1936, **33**, 294).—Cyclostyle paper backed by a piece of filter-paper makes a satisfactory rapid ultrafilter medium. S. C.

Collodion membranes. Preparation, physical properties, and dialysis measurements in solutions. V. Nowatke (Kolloid-Z., 1936, **75**, 269—284).—The influence of method of prep. on the thickness, H_2O content, and H_2O-permeability of collodion membranes has been determined. With increasing η of the collodion solution, the membranes formed become thinner, more elastic, and stronger. Max. permeability is attained when a definite amount of air is used to remove the solvent. The extent to which the permeability of the membrane is altered by adding different org. compounds to the collodion solution has been determined. Dialysis measurements with alkali chloride and $CO(NH_2)_2$ solutions are reported. The dialysis consts. tend to rise with increasing at. wt. of the cation and are in agreement with the lyotropic series (except Cs). Diffusion coeffs. have been calc. from the dialysis consts. E. S. H.

Emulsifier. K. Fischer (Kolloid-Z., 1936, **75**, 285—287).—Laboratory apparatus is described. E. S. H.

Immersion pyknometer. W. Jung (J. Indian Chem. Soc., 1936, **13**, 136—137).—A pyknometer specially adapted for obtaining the *d* of powders is described. The usual difficulty of weighing under H_2O is met by evacuating the pyknometer in a desiccator and allowing H_2O to flow into the desiccator until the pyknometer is filled. C. R. H.

Surface tension. C. C. Patel, K. V. Desai, and S. M. Mehta (J. Univ. Bombay, 1935, **4**, Part II, 132—139).—Methods of measuring surface tension are discussed critically. A modification of Ferguson's method (A., 1932, 828) which increases accuracy is described, and is illustrated with data for $CaCl_2$ solutions. J. W. S.

Impulse vacuum meter. A. Butschinski (Tech. Phys. U.S.S.R., 1936, **3**, 223—228).—An apparatus for measuring pressures of 10^{-4}—approx. 2×10^{-3} mm. by means of the impulse frequency of a thyraton is described. The frequency is a linear function of the pressure. R. S. B.

Reaction vessels of variable capacity. L. Ramberg (Z. physikal. Chem., 1936, **176**, 289—294).—These consist of two flat-bottomed glass tubes sliding one within the other. R. C.

Combustion experiment. S. C. Blacktin (Chem. and Ind., 1936, 402—403). D. K. M.

Weights and balances in ancient Egypt. Anon (Nature, 1936, **137**, 890—892). L. S. T.

Thirty years of chromatography. L. Zechmeister and L. von Cholnoky (Monatsh., 1936, 68, 68—80).—A historical and descriptive summary. F. L. U.

Geochemistry.

Temperatures and constituents of the upper atmosphere. D. F. Martyn and O. O. Pully (Proc. Roy. Soc., 1936, **A**, **154**, 455—486; cf. Proc. Phys. Soc., 1935, **47**, 340).—Temp. between the *E'* and *F* regions of the ionosphere are found, from consideration of the electron collision frequencies, to reach vals. of the order 1000° abs., both in summer and in winter daytime. Considerable cooling of the upper atm. occurs during the night, and from the observed rate of cooling it is found that an average concn. of 1 part in 6000 by vol. of H_2O vapour is present in the ionosphere. The high temp. found are attributed mainly to the absorption of solar ultra-violet energy by O_3. The attachment of electrons to neutral particles is the chief process by which free electrons are renewed from the ionised regions. L. L. B.

Abalach soda lake in Jakutia. A. D. Egorov and V. I. Nikolaev (J. Appl. Chem. Russ., 1936, **9**, 665—669).—The H_2O contains Na_2CO_3 3·46, $NaHCO_3$ 2·20, and NaCl 3·22%. It can be exploited by pumping out the H_2O before the ice melts in the spring, and further concn. by a combination of freezing and evaporation. R. T.

Can the difference in density between sea- and fresh water be accounted for by fractional distillation of the isotopic forms of water? K. Neumann and G. Tohmfor (Z. physikal. Chem., 1936, **176**, 226—228).—It is calc. that the *d* of sea-H_2O will exceed that of the first fraction on isothermal distillation at 20°, which may be regarded as equiv. to fresh H_2O, by $4·3 \times 10^{-6}$. A *d* difference of $2·9 \times 10^{-6}$ between sea- and fresh H_2O has been observed experimentally (cf. A., 1935, 600). R. C.

Heavy metals in mineral waters. II. S. Miholić (Bull. Soc. Chim. Yougoslav., 1935, **6**, 217—234).—Natural H_2O containing U or its degradation products is characteristic of the earlier, and those containing Co and Ni of the later, Archean folding. R. T.

Conductivity of mineral waters. II. Mineral water of Rogaška Slatina. P. S. Tutundzić (Bull. Soc. Chim. Yougoslav., 1935, **6**, 205—215).—Conductivity and other data are recorded. R. T.

Arsenic, nickel, cobalt, silver, bismuth, and uranium ores in calcite veins in the Riesengebirge. K. Hoehne (Chem. Erde, 1936, **10**, 432—474).—Chemical analyses of the ores from different veins in the Bergfreiheit mine at Oberschmiedeberg in Silesia are given, and the several minerals present are identified in polished sections. L. J. S.

Nature of the calcium content of Thuringian iron ores. J. Holzner (Chem. Erde, 1936, **10**, 409—431).—Analyses of different fractions of two oolitic ores from Schmiedefeld show that the chloritic mineral is thuringite. Ca is present as a silicate with the approx. formula $Ca_2Al_2SiO_7$, seen in microsections as a colourless (orthorhombic?) granular aggregate, which cannot be identified with any known mineral species. P is present mainly as Fe phosphate. L. J. S.

Metamorphosed Devonian phyllites in the Altvatergebirge. R. Fabian (Chem. Erde, 1936, **10**, 343—408; Diss., Breslau, 1936).—Geological and petrographical description with chemical analyses of the rocks. L. J. S.

Formation of kaolin and alumina from granite and gneiss. F. W. Freise (Chem. Erde, 1936, **10**, 311—342).—The weathering of granite and gneiss in Brazil by the action of CO_2 and humic acids gives rise to both kaolin and bauxite or laterite. The action of CO_2 and formic, lactic, and acetic acids on these materials was examined. L. J. S.

Petrological classification of the basic intrusives of Danta state (H. Gujrat). N. L. Sharma and N. C. Nandy (Proc. Indian Acad. Sci., 1936, **3**, **B**, 366—376). A. G. P.

New synthesis of langbeinite, vanthoffite, and polyhalite. K. H. Ide (Kali, 1935, **29**, 83—86, 93—96, 103—105; Chem. Zentr., 1935, ii, 1522—1523).—K, Na, and Ca sulphates react in the solid state with $MgSO_4$ at temp. $\nless$ 80°, giving langbeinite, vanthoffite, and polyhalite, respectively, in amounts recognisable by *X*-ray methods. The reaction is promoted by compressing the mixture. KCl similarly reacts with $MgSO_4$, giving either langbeinite or anhydrokainite, but formation of glauberite or glaserite was not detected. J. S. A.

Geochemistry of selenium. II. V. M. Goldschmidt and L. W. Strock (Nachr. Ges. Wiss. Göttingen, 1935, [ii], **1**, 123—142; Chem. Zentr., 1935, ii, 1522; cf. A., 1934, 53).—The S : Se ratio in meteorites, deep-seated basic rocks, sulphide and arsenide ores, sedimentary rocks, and marine and lacustrine salt deposits is discussed. Pneumatolytic and high hydrothermal sulphides and arsenides contain relatively more Se than the deeper-seated ores. An enrichment of Se is found with Cu in sulphide ore deposits, and with Fe and Mn in oxidic sediments, but FeS_2 from sedimentary rocks is very poor in Se. J. S. A.

Selenium content of European and Japanese slates. E. Minami (Nachr. Ges. Wiss. Göttingen, 1935, [ii], **1**, 143—145; Chem. Zentr., 1935, ii, 1522).—Data are recorded. J. S. A.

Occurrence of selenium in natural phosphates, superphosphates, and phosphoric acid.—See B., 1936, 493.

Native blue rock-salt. IV. Rate of growth and colour. K. Przibram (Sitzungsber. Akad. Wiss. Wein, IIa, 1934, **143**, 489—497; Chem. Zentr., 1935, ii, 1504).—Blue native NaCl crystals have a deeper blue colour in the portions giving evidence of most rapid growth, and a lighter more violet colour in regions of slower growth. The effect is attributed to lattice distortion, more impurities, causing the inclusion of layer Na particles, being included where growth was rapid. A similar effect is given by artificially coloured crystals. J. S. A.

Characterisation of nontronite ferrisilicates. Marinsk nontronites. I. J. Mikei (Ukrain. Chem. J., 1936, **11**, 56—66).—Most of the H_2O in nontronite (I) is adsorbed on colloidal constituents; the chemically bound H_2O is eliminated at 550—660°. Adsorption by (I) of different dyes is studied. R. T.

Disthene (cyanite) from Prilepec in the Selečka mountains. L. Barić (Z. Krist., 1936, **93**, 57—92).—Mineralogical. Different specimens of the mineral are described, and goniometric data, refractive index, double refraction, extinction, pleochroism, twinning, and chemical composition are given in detail. B. W. R.

Mineralisation of the Virginia titanium deposits. C. S. Ross (Amer. Min., 1936, **21**, 143—149).—The deposits occur within a rock of the anorthosite type introduced as a mush of crystals. The ores and associated gangue minerals were deposited by invading solutions probably derived from a highly ferromagnesian rock which was a differentiate from the same primary magma as the anorthosite. The outstanding chemical factors of mineralisation are indicated. L. S. T.

Helium ratios of rocks and minerals from the diamond pipes of South Africa. A. Holmes and F. A. Paneth (Proc. Roy. Soc., 1936, A, **154**, 385—413).—He ratios have been obtained for 20 specimens of rocks and minerals with the object of determining the relative ages of the inclusions found in kimberlite. The technique of He determination and of U and Th determinations is described. The He ratio of kimberlite, corresponding with an age of 58×10^6 years, is consistent with the late Cretaceous age assigned to the diamond pipes. Xenoliths of the amphibolite group, known to be of Pre-Cambrian age, have He ratios of a higher order than kimberlite. Xenoliths of the peridotite suite (including zircons) give low He ratios. The bearing of the results on theories of petrogenesis is discussed. L. L. B.

Viscosity of molten lavas from Mount Alaghez. M. P. Volarovitsch, D. M. Tolstoi, and L. I. Kortschemkin (Compt. rend. Acad. Sci. U.R.S.S., 1936, **1**, 333—336).—η of basalt, andesito-basalt, andesite, dacite, and alkaline dacite was determined by the rotating-cylinder method. The effect of temp. on η was also determined. η increases with increase of acidity of the rocks. A. J. M.

Spectrum analysis of blende by pyroelectric concentration. S. Piña de Rubies and J. M. López de Azcona (Anal. Fis. Quím., 1936, **34**, 307—314).—Analysis of blende from Picos de Europa (cf. Llord *et al.*, A., 1911, ii, 733) by the author's procedure (A., 1934, 1323) reveals the presence of Ni, Co, Mn, Mo (?), Mg, Al, Si, Ca, Na, P, Cr, Ti, V, Ba, and Be. The procedure is more rapid than chemical methods, and avoids the possibility of detecting elements arising from impure reagents. Previous work on the analysis of blendes is summarised. F. R. G.

Cleavage of ionic minerals. M. D. Shappell (Amer. Min., 1936, **21**, 75—102).—Mineral cleavage is resolved into two components, viz., optical effect and cleavability which is the chief component and for which a quant. expression has been deduced. Application to minerals the constituent atoms of which have inert-gas cores gives good agreement with observation. L. S. T.

Dickite in Missouri. W. A. Tarr and W. D. Keller (Amer. Min., 1936, **21**, 109—114).—Dickite (I) occurs in three localities near Columbia, Missouri, and in the Pb ores at Flat River, S.E. Missouri. Two of the former localities are limestone quarries in which (I) occurs in chert in association with millerite, chalcopyrite, galena (II), pyrite, and wurtzite. The associated country rock contains sphalerite and barite. (I) from the Pb ores is associated with marcasite and (II), and is a replacement of the dolomite country rock. Optical properties are recorded. L. S. T.

Crystal form of sternbergite. M. A. Peacock (Amer. Min., 1936, **21**, 103—108).—Remeasurement of crystals of sternbergite, $AgFe_2S_3$, from Joachimsthal, Bohemia, shows that the classical data are inadequate. The crystals are orthorhombic, dipyramidal with $a:b:c=0·5913:1:0·6250$. The morphology is similar to that of cubanite, $CuFe_2S_3$, but a close systematic relation between the two species has yet to be established. L. S. T.

Composition of clay substance. R. Schwarz and G. Trageser (Z. anorg. Chem., 1936, **227**, 179—183).—Very pure Zettlitz kaolin (I) still contains at least 10% of admixed felspar and mica which can be converted into kaolin by hydrothermal treatment. The H_2O content of a specimen of (I) has thus been raised to 1·76 mol. per formula-wt., and the inference drawn by Körner and others (this vol., 50) from the results of isothermal dehydration of (I) is therefore invalid. F. L. U.

Fluorescent minerals. M. Déribéré (Ann. Chim. Analyt., 1936, [iii], **18**, 117—119).—The characteristic fluorescence of autunite, blende, willemite, chalcolite, celestine, scapolite, calcite, gypsum, aragonite, sodalite, sylvine, fluorite, and rock-salt is described. J. S. A.

Plagioclase and its determination in pegmatites. D. Beljankin and V. Onisimo-Janovski (Trans. Res. Inst. Ceram., 1934, No. 43, 10—19).—The occurrence of plagioclase and methods for its microscopic determination in pegmatites are discussed. Ch. Abs. (*e*)

Dioritic intrusive rocks and contact metamorphism in the Cascade Range in Oregon. A. F. Buddington and E. Callaghan (Amer. J. Sci., 1936, [v], **31**, 421—449).—Petrographical descriptions and chemical analyses of augite-diorite, augite-dacite-porphyry, aplite, granite, etc. are given. These rocks are intrusive into volcanic rocks which in places are changed into tourmaline-hornfels. L. J. S.

Fluorite in Aberdeenshire and Banffshire. A. Russell (Min. Mag., 1936, **24**, 307—317).—Details are given of the occurrence of fluorite at several localities. L. J. S.

Baryte from Manvers Main colliery, Yorkshire. A. Russell (Min. Mag., 1936, **24**, 318—320).—A crystallographic description is given of well-developed crystals from a cavity in sandstone. Analysis by C. P. Finn (1930) gave $BaSO_4$ 98·50, $CaSO_4$ 0·65, $SrSO_4$ 0·18, ignition loss 0·33%. L. J. S.

Wulfenite from Cumberland and leadhillite from Kirkcudbrightshire. A. Russell (Min. Mag., 1936, **24**, 321—323).—New occurrences of these rare minerals are noted. L. J. S.

Ettringite from Scawt Hill, Co. Antrim. F. A. Bannister [with M. H. Hey and J. D. Bernal] (Min. Mag., 1936, **24**, 324—329).—Minute crystals of ettringite from the larnite-rock in the contact-zone of chalk and dolerite (A., 1934, 1197) have a hexagonal unit cell, *a* 11·24, *c* 21·45 A. (*c*/*a* 1·908), containing $Ca_{12}Al_4(OH)_{24}(SO_4)_6,52H_2O$. They are identical with crystals from the original locality (Ettringen, Laacher See, Rhine) and with artificial crystals from Portland cement. ω 1·4655, ε 1·4618, *d* 1·772. The space-group is D_{4h}^{6}, and a structure of the zeolitic type with $48H_2O$ in channels parallel to the *c*-axis is suggested. At 110° 34·4% H_2O is lost and the structure partly collapses, leaving an oriented pseudomorph of cell dimensions *a* 8·4, *c* 10·21 A. and the same space-group. L. J. S.

Petrochemistry of granites of Tarpatak Valley of High Tátra. E. Lengyel (Föld. Közlöny, 1935, **65**, 120—126).—Granitic rocks are characterised by the changeable ratio of the contents of alkali or alkali–lime felspars. Some granites approach the Si-rich granitic magma in composition. Ch. Abs. (*e*)

Phosphatic limestone of the lower Eocene of the East Fergana (Middle Asia). A. V. Peive (Bull. soc. nat. Moscou, Sect. geol., 1933, **11**, 385—404).—The most probable explanation is that the phosphates are due to bacterial activity in sea-H_2O with a low $[P_2O_5]$. Ch. Abs. (*e*)

Distribution and mineralogical classification of the decomposed pumices in the north-western part of Kwanto district, Japan. M. Harada (J. Sci. Soil Manure, 1935, **9**, 54—62, 189—201).—Soils from the decomp. of pumice are classified into 4 groups, according to the kind and quantity of hypersthene, augite, hornblende, quartz, and small pieces of lava. Ch. Abs. (*e*)

Study of [petroleum] source beds in late Mesozoic rocks on the west side of the Sacramento Valley, California. P. D. Trask and H. E. Hammar (Bull. Amer. Assoc. Petr. Geol., 1934, **18**, 1346—1373).—Analytical data are recorded. Ch. Abs. (*e*)

Metamorphism of organic sediments and derived oils. D. White (Bull. Amer. Assoc. Petr. Geol., 1935, **19**, 589—617).—A discussion. Ch. Abs. (*e*)

Carbon ratios in part of Arkansas–Oklahoma coal field. T. A. Hendricks (Bull. Amer. Assoc. Petr. Geol., 1935, **19**, 937—947). Ch. Abs. (*e*)

Organic Chemistry.

Highly polymerised compounds. CXXXX. Development of macro-molecular chemistry. H. Staudinger (Ber., 1936, **69**, [*B*], 1168—1185).—Mainly historical. Reply is made to Meyer *et al.* (this vol., 586). H. W.

Synthesis of hydrocarbons of the aliphatic series. A. D. Petrov (Uspechi Chim., 1934, **3**, 1050—1077).—A review. Ch. Abs. (*r*)

Initial formation of alcohols during slow combustion of methane and ethane.—See this vol., 801.

Slow combustion of methane, methyl alcohol, formaldehyde, and formic acid.—See this vol., 801.

Catalytic cyclisation of aliphatic hydrocarbons. B. Moldavski and H. Kamuscher (Compt. rend. Acad. Sci. U.R.S.S., 1936, **1**, 355—359).—Paraffins are cyclised and dehydrogenated to the corresponding aromatic hydrocarbons (% yields in parentheses) by passing them over Cr_2O_3 (prep. described) at > 400°. Very little olefine formation occurs, the gaseous products consisting mainly of H_2 (74—94%) and some C_nH_{2n+2}. Thus n-C_6H_{14}, n-C_7H_{16}, n-C_8H_{18} (or C_8H_{16}), $(Bu^\beta)_2$, di-*iso*amyl, and $PhBu^\alpha$ give, respectively, C_6H_6 (17), PhMe (26), *o*-xylene (63), *p*-xylene (36), m-$C_6H_4MePr^\beta$, and $C_{10}H_8$ (12). Of other catalysts tried only MoS_2 was similarly effective. J. W. B.

High-temperature pyrolysis of gaseous olefines. H. Tropsch, C. I. Parrish, and G. Egloff (Ind. Eng. Chem., 1936, **28**, 581—586).—The pyrolysis of C_2H_4, C_3H_6, and Δ^α-, Δ^β-, and *iso*-butene was studied at 1100° and 1400° and at 50 mm. pressure with a contact time (*t*) of 0·0008—0·044 sec. The rate of decomp. increased more rapidly with *t* for C_3H_6 and the butenes than for C_2H_4, indicating the greater thermal resistance of C_2H_4. C_2H_2 was one of the principal products of the pyrolysis, the amount increasing with rise of temp. The yields of paraffins were > 25% by vol. except in the case of C_2H_4 and C_3H_6. H_2 was an important product at high vals. of *t* in all pyrolyses, the yield increasing with *t*. In the pyrolysis of Δ^α- and Δ^β-butene at 1100° a greater yield of butadiene was obtained for the latter, whereas *iso*butene gave approx. 54% less butadiene and 50% more C_2H_2 than Δ^β-butene. No evidence of the isomerisation of Δ^α- or Δ^β-butene to *iso*butene was obtained. In all pyrolyses liquid products and C were formed in varying amounts. The severe conditions of pyrolysis completely masked the primary products because of extensive decomp., but experimental] data and theoretical considerations indicate that the decomp. of olefines is preceded by polymerisation and that the gaseous products are produced by secondary reaction. H. C. M.

Catalytic hydration of olefines. II. Hydration of propylene over liquid catalysts at atmospheric pressure. E. K. Remiz (J. Appl. Chem. Russ., 1936, 9, 703—710).—$Pr^{\beta}OH$ is obtained in 21% yield from $CH_2{:}CHMe$, in presence of 54% H_2SO_4 containing 3% of Ag_2SO_4, at 110°. Apparatus for the continuous production of $Pr^{\beta}OH$ by the above method is described. R. T.

Polymerisation of propylene. Catalytic action of zinc chloride. O. L. Brandes, W. A. Gruse, and A. Lowy (Ind. Eng. Chem., 1936, 28, 554—559).—The formation of liquid polymerides when C_3H_6 is heated in presence of $ZnCl_2$ depends on the pressure, temp., and duration of reaction. A max. yield of 81·5% is obtained at 260—270° and 3225 lb. per sq. in. during 75 min.; very little reaction occurs in the absence of $ZnCl_2$. At lower temp., the fraction of b.p. $< 200°$ increases (up to 92% of the total liquid), the tripolymeride being the main product together with smaller amounts of C_{10-12} hydrocarbons. The product obtained at 290—310° contains considerable amounts of C_{5-12} hydrocarbons, principally olefines and paraffins. The presence of naphthalenes is suspected. J. L. D.

Kinetics of *cis–trans* isomerisations.—See this vol., 802.

Preparation and physical constants of β-methyl-Δ^α^-butene. M. L. Sherrill and G. F. Walter (J. Amer. Chem. Soc., 1936, 58, 742—745).—$CH_2Br{\cdot}CHBr{\cdot}OEt$ and MgMeCl give β-ethoxypropyl bromide, b.p. 28·6—28·8°/10 mm., 138—138·1°/760 mm., converted by a large excess of KOH at 110—150° into $CH_2{:}CMe{\cdot}OEt$, b.p. 61·2—61·8°/760 mm. Successive treatment of this with Br and MgEtBr in Et_2O affords β-ethoxy-β-methylbutyl bromide, b.p. 53·4—53·6°/9·5 mm., which with Zn dust+Zn–Cu in 95% EtOH affords β-methyl-Δ^{α}-butene (I), b.p. 31·05±0·05°/760 mm. (dibromide, b.p. 47·4—48°/8·5—9 mm.). The ultra-violet absorption spectra of (I), $CHMe{:}CMe_2$, and Δ^{α}- and Δ^{β}-pentene are given. Physical data for these hydrocarbons and $CH_2{:}CHPr^{\beta}$ are recorded. H. B.

Raman spectra of β-methyl-Δ^{α}- and -Δ^{β}-butene. D. D. Thompson and M. L. Sherrill (J. Amer. Chem. Soc., 1936, 58, 745—747; cf. Bourguel and Piaux, A., 1932, 1189).—Comparison of the spectra of β-methyl-Δ^{α}-butene (I) and the low (*A*) and high (*B*) fractions of the hydrocarbon obtained by dehydration of *tert.*-amyl alcohol shows that (*B*) is practically pure β-methyl-Δ^{β}-butene (II) whilst (*A*) is a mixture of (I) and (II). H. B.

Fission and isomerisation of olefines involving a tertiary radical. I. N. Nazarov (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 329—332).—The following are prepared from MgRX and the appropriate ketone: $CMePr^{\beta}Bu^{\gamma}{\cdot}OH$ (Whitmore *et al.*, A., 1933, 1140), *ββδ-trimethyl-γ-ethyl-*n*-pentan-γ-ol*, b.p. 188—191°, *ββγ-trimethyl-*n*-hexan-γ-ol*, b.p. 170—172°, *γ-*tert.*-butyl-*n*-pentan-γ-ol*, b.p. 172—175° $CMeEtBu^{\gamma}{\cdot}OH$, and $CMe_2Bu^{\gamma}{\cdot}OH$. They are converted by dehydration (2-$C_{10}H_7{\cdot}SO_3H$ or I), respectively, into $CPr^{\beta}Bu^{\gamma}{:}CH_2$ (I), *δδ-dimethyl-γ-*iso*propyl-Δ^{β}-pentene* (II), b.p. 153—158°, *ββγ-trimethyl-Δ^{γ}-hexene* (III), b.p. 130—132°, *γ-*tert.*-butyl-Δ^{γ}-pentene* (IV), b.p. 124—132°, $CMeBu^{\gamma}{:}CHMe$ (V), and $CMeBu^{\gamma}{:}CH_2$ (VI). Fission of (I) with 1:4-$C_{10}H_6Br{\cdot}SO_3H$ at 130° affords $CMe_2{:}CH_2$ and $CHMe{:}CMe_2$; (II) similarly gives $CMe_2{:}CH_2$, $CHMe{:}CHPr^{\beta}$, and $CHEt{:}CMe_2$, the assumed mechanism being the isomerisation of a liberated substituted vinyl radical. (III)—(VI) do not undergo fission. J. W. B.

Condensation of acetylene and acetic acid.—See this vol., 807.

Preparation of dialkylacetylenes from acetylenic Grignard reagents and alkyl sulphates. S. D. Thorn, G. F. Hennion, and J. A. Nieuwland (J. Amer. Chem. Soc., 1936, 58, 796—797).—$CMe{:}CAlk$ and $CEt{:}CAlk$ are prepared in good yield from $CAlk{:}C{\cdot}MgBr$ (I) (1 mol.) and Me_2SO_4 and Et_2SO_4 (2 mols.), respectively. The following are described: methyl-butyl-, b.p. 110—111°/747 mm., and -hexyl-, b.p. 155—156°/747 mm.; ethyl-butyl-, b.p. 129—130°/747 mm., -amyl-, b.p. 153—155°/745 mm., and -vinyl-, b.p. 83°/747 mm., -acetylenes. (I) do not react with alkyl halides; reaction could not be catalysed by various metals and/or their salts. H. B.

Raman spectra of solid ethylene halides.—See this vol., 776.

Photochemical formation of ethylene iodide.—See this vol., 688.

Decomposition of ethylene oxide.—See this vol., 802.

Preparation of α-chloro-γ-bromopropane, and the velocity of addition of hydrogen bromide to allyl chloride. M. S. Schostakovski (J. Appl. Chem. Russ., 1936, 9, 681—683).—$CH_2Cl{\cdot}CH_2{\cdot}CH_2Br$ (I) and $CHMeCl{\cdot}CH_2Br$ are obtained in equal amount from $CH_2{:}CH{\cdot}CH_2Cl$ and HBr at 0°; at −19°/1·5—2 atm. (I) alone is obtained, in 90% yield. R. T.

Substitution and inversion of configuration.—See this vol., 803.

Catalytic esterification of alcohols.—See this vol., 806.

Exchange reactions between heavy water and hydrogen compounds. E. Ogawa (Bull. Chem. Soc. Japan, 1936, 11, 310—320).—A substance, RH, is dissolved in H_2O containing 49 mol.-% of D_2O, allowed to come to equilibrium (some RD formed), distilled, and the *d* of the distillate measured. Thus are calc. $K_m=[RD][H_2O]/[RH][HDO]$. K_m are 10—16% too high owing to fractionation and further reaction during distillation. Determinations with 24 substances give the following K_m at 100°: OH (alcoholic) 1·55 or 0·72 (1·19 *at* 50°), (NH_2OH,HCl) 0·8, (H_3BO_3) 0·46, (H_3PO_4) 0·34; NH (NH_4Cl) 0·52

(0·45 at 50°), [$CO(NH_2)_2$] 0·50 (0·71 at 50°); CO_2H ($H_2C_2O_4$) 0·51 (0·62 at 50°), (succinic) 0·42, (maleic) 0·66, ($NaHC_2O_4$) 0·91, (Na H succinate) 0·4; HSO_4' 0·1; OH′ (NaOH) 0·2. K_m gives a measure of the differences of zero point energies or of the chemical binding forces of RH and RD. The results do not favour co-ordination between OH and CO_2H of OH-acids nor the usual betaine formula of NH_2-acids.

R. S. C.

Catalytic properties of rhenium. II. Dehydrogenation of the propyl alcohols. M. S. Platonov, S. B. Anissimov, and V. M. Krasche-ninnikova (Ber., 1936, 69, [*B*], 1050—1053; cf. A., 1935, 830).—Dehydrogenation of $Pr^{\alpha}OH$ is effected as efficiently by Re at 400° as by an equal column of Cu at 300°. Re causes only very slight decomp. of the EtCHO produced and does not dehydrate $Pr^{\alpha}OH$. The formation of solid or liquid by-products could not be detected. The catalyst retains its activity well. $Pr^{\beta}OH$ is more efficiently dehydrogenated to $COMe_2$ by Re than by Cu and only slight decomp. of $COMe_2$ is observed at $> 500°$.

H. W.

Isomeric forms of the optically active αγ-dimethylallyl alcohols [Δ^{γ}-penten-β-ols]. H. W. J. Hills, J. Kenyon, and H. Phillips (J.C.S., 1936, 576—583).—The H phthalate, m.p. 90—90·5°, of *dl*-CHMe:CH·CHMe·OH gives the brucine salt, m.p. 169—169·5°, $[\alpha]_{5461}$ −15·2° in EtOH, and thence the H ester (I), m.p. 82—84°, $[\alpha]_{5893}$ +38·75° in Et_2O, of the (+)-alcohol (II); the mother-liquors give the *brucine* salt, m.p. 157—159°, and thence the *H phthalate* (III), m.p. 82—84°, $[\alpha]_{5893}$ −24·1° in $CHCl_3$, of the (−)-alcohol (IV). Hydrolysis of (I) and (III) gives (II) and (IV) of varying α. [α] of (III) is recorded in 7 solvents; (III) is usually dextrorotatory, about $[\alpha]_{5461}^{20}$ +0·84°, but α changes with time often to negative; [α] also has a very high temp. coeff., changing to negative at about 30—40°. (IV) behaves similarly when kept, α often decreasing numerically. The changes with time are very erratic and could not be controlled. The optical behaviour of the esters and ethers is, however, quite normal; the following are prepared from (II): *formate*, b.p. 122—123°, $[\alpha]_{5461}^{20}$ −72·8°; *acetate*, b.p. 136—137°, $[\alpha]_{5461}^{20}$ −76·1°; *benzoate*, b.p. 126°/13 mm., $[\alpha]_{5461}^{20}$ +26·5°; o-, b.p. 124—125°/< 0·1 mm., $[\alpha]_{5461}^{20}$ +29·9°, m-, b.p. 126—127°/< 0·1 mm., $[\alpha]_{5461}^{20}$ +27°, and p-*nitrobenzoate*, m.p. 48°, $[\alpha]_{5461}$ +57·3° in H_2O; *Me* (by MeI on the K salt in Et_2O), b.p. 90°, $[\alpha]_{5461}^{20}$ −56°, *Bu*$^{\alpha}$, b.p. 149—150°, $[\alpha]_{5461}^{20}$ −30·4°, and *CH_2Ph ether*, b.p. 107°/11 mm., $[\alpha]_{5461}^{20}$ −145·6°. (IV) with $MeOH–H_2SO_4$ gives a *Me ether*, b.p. 90—91°, $[\alpha]_{5461}^{20}$ −1°, but with $Bu^{\alpha}OH–H_2SO_4$ the dl-*Bu*$^{\alpha}$ *ether*, b.p. 150—151°. The parachor of (II), (IV), and the *dl*-alcohol varies, but is always very low; CH_2:CH·CHEt·OH, CH_2:CH·$CHBu^{\alpha}$·OH, and CHPh:CH·CH_2·OH also have very low parachors, but that of CH_2:CH·CH_2·OH is normal. The above and some other abnormalities are mostly explained by assuming that (II), (IV), etc. are in equilibrium with large but varying amounts of the cyclic form,  $CHMe<\overset{CH_2}{\underset{O}{}}>CHMe$ (or its analogues). This, however, does not explain many other facts, notably that (II) gives esters of normal, or almost normal, [α] after "mutarotation" has occurred. *Cis–trans* isomerism explains only a few of the abnormalities. Hydrogenation (PtO_2) of (II) in Et_2O affords (+)-pentan-β-ol, b.p. 118—119° (H phthalate, m.p. 34°, $[\alpha]_{5893}$ +35·9° in $CHCl_3$). (II) gave a (−)-chloride, b.p. 20°/13 mm., which with $CaCO_3$ in H_2O gives a (−)-alcohol, but it is impossible to state whether this is related to (II) or to (IV).

R. S. C.

Dehydration of dimethyl*cyclo*butylcarbinol. B. A. Kasanski (Ber., 1936, 69, [*B*], 950—954).—Dimethyl*cyclo*butylcarbinol, from Et *cyclo*butylcarboxylate or acetyl*cyclo*butane (I) and MgMeI, is dissolved in decahydronaphthalene and treated successively with K, CS_2, and MeI and the solution is heated. The product contains *iso*propylidene*cyclo*butane (oxidised to $COMe_2$), α-methylvinyl*cyclo*butane [oxidised to (I)], a glycol, and possibly succinic acid. Catalytic hydrogenation of the mixture affords iso*propyl*cyclo-*butane*, b.p. 90·5—91·5°/750 mm.

H. W.

Secondary acyclic alcohols with seven to ten carbon atoms. M. Tuot (Compt. rend., 1936, 202, 1339—1340).—The appropriate aldehydes (prep. from the alcohols by Cu reduced very slowly at 250—265°) and Grignard reagents give 60—85% yields of heptan-δ-ol, b.p. 70°/25 mm., β-methylhexan-ε-ol, b.p. 74°/28 mm., octan-δ-ol, b.p. 81°/17 mm., β-methylheptan-γ-ol, b.p. 73°/19 mm., βε-dimethylhexan-γ-ol, b.p. 64°/15 mm., nonan-γ-ol, b.p. 93°/18 mm., β-methyloctan-δ-, b.p. 91°/23 mm., and -ε-ol, b.p. 79°/15 mm., βζ-dimethylheptan-γ-, b.p. 88°/25 mm., and -δ-ol, b.p. 79°/15 mm., and *βη-dimethyloctan-δ-ol*, b.p. 96°/18 mm. Other physical data are given.

R. S. C.

Reaction of etherates of tin and titanium tetrachloride. I. Action of thionyl chloride on the etherates. J. L. Goldfarb and L. M. Smorgonski (Ber., 1936, 69, [*B*], 1036—1039).—$SnCl_4$ or $TiCl_4$ is added to a mixture of the ether and $SOCl_2$ at 0° followed by warming on the water-bath. Et_2O affords EtCl (1·5 mols.), reaction proceeding: $Et_2O+SOCl_2 \rightarrow EtCl+OEt{\cdot}SOCl$ (I) and (I) $\rightarrow EtCl+SO_2$. Di*iso*amyl ether yields $C_5H_{11}Cl$, but side reactions cause evolution of HCl and production of a substance containing S. $CH_2Ph{\cdot}OEt$ gives EtCl, much HCl, and an amorphous substance devoid of S or Cl. PhOEt yields SO_2, much HCl, EtCl, and a material containing S which is sol. in alkali. Et_2O and S_2Cl_2 afford EtCl, SO_2, and S.

H. W.

Thermal decomposition of ethylene oxide. H. W. Thompson and M. Meissner (Nature, 1936, 137, 870—871).—Results of a more detailed investigation (cf. A., 1929, 1243) are summarised. Over the range 435—505°, CO and CH_4 are the main products of the reaction, but H_2 and C_2H_6 are also formed. The variation of *k* with pressure indicates that the reaction involves the superposition of several independent quasi-unimol. processes. The existence of appreciably long reaction chains is improbable.

L. S. T.

Dioxan series. III. Use of zinc and cadmium chlorides in Grignard synthesis of alkyl-substituted dioxans. R. K. Summerbell and L. N. Bauer (J. Amer. Chem. Soc., 1936, 58, 759—761).—

Improved yields of 2 : 3-dialkyldioxans (cf. this vol., 341) are obtained from 2 : 3-dichlorodioxan (I) and MgAlkBr when the latter is first treated with 1 mol. of anhyd. $ZnCl_2$ or $CdCl_2$ and the Et_2O replaced by PhMe. The following are described: 2 : 3-*dimethyl-* (? 2 forms), b.p. 127·7—129°/750·8 mm. and 132·2—132·7°/750·8 mm., 2 : 3-*diethyl-*, b.p. 166·5—168·5°/739 mm., 2 : 3-*di*-n-*propyl-*, b.p. 87°/12 mm., 202—205°/744 mm., 2 : 3-*di*-n-*butyl-*, b. p. 129—130°/22 mm., 238—240°/744 mm., and 2 : 3-*diallyl-*, b.p. 90·2—90·7°/16 mm., -*dioxans*. The gases evolved in the reaction of (I) with Et_2O–MgMeBr are CH_4 (5·4%), C_2H_6 (94%), and C_2H_4 (0·6%). H. B.

Effect of propyl alcohol on hydrolysis of sulphuric acid esters.—See this vol., 804.

Action of molybdic acid on lævorotatory α-glycerophosphoric acid. P. FLEURY (J. Pharm. Chim., 1936, [viii], 23, 541—545).—The lævorotation of α-glycerophosphoric acid depends on the p_H; it is max. at p_H 8·0. In presence of $(NH_4)_6Mo_7O_{24}$, the rotation becomes positive, with a max. at p_H 4·3—4·5, at which acidity glycerophosphomolybdates are most stable (cf. A., 1932, 143). E. W. W.

Esters of thiosulphurous acid $S_2(OR)_2$. A. MEUWSEN (Ber., 1936, 69, [*B*], 935—937; cf. A., 1935, 326).—In agreement with Stamm (A., 1935, 729) the greenish-yellow series of esters is regarded as non-existent, but isomerides OR·S·S·OR and $R·SO_2·SR$ exist. The production of colourless $S_2(OEt)_2$ from S_2Cl_2 necessitates the use of an excess of NaOEt. $S(OEt)_2$ is stable towards air and SeO_2 at room temp., whereas NO_2, O_3, or H_2O_2 causes separation of S. MgEtBr causes production of a little Et_2S_2 without separation of S. Hydrolysis by cold *N*-KOH–MeOH produces S and $K_2S_2O_3$. Thermal decomp. probably occurs thus: $S_2(OEt)_2 \rightarrow H_2S + S + EtOAc$. H. W.

Sulphur monoxide diethylacetal, $S(OEt)_2$ [ethyl sulphoxylate]. A. MEUWSEN and H. GEBHARDT (Ber., 1936, 69, [*B*], 937—946).—Catalytic decomp. of $S_2(OEt)_2$ by NaOEt in EtOH affords *Et_2 sulphoxylate*, $S(OEt)_2$, b.p. 35°/32 mm., 117°/733 mm., readily autoxidised at room temp. to Et_2SO_3, also obtained by use of NO_2 in abs. Et_2O, $KMnO_4$ in $COMe_2$, or SeO_2; even O_3 does not produce Et_2SO_4. Hydrolysis by KOH–MeOH proceeds mainly thus: $2S(OEt)_2+3KOH=K_2S_2O_3+3EtOH+KOEt$, small amounts of K_2S and K_2SO_3 being also produced. With Cu_2O at 110° $S(OEt)_2$ affords a mixture of oxides and sulphides of Cu with some MeCHO. In a sealed tube at 130° $S(OEt)_2$ becomes carbonised with production of S and SO_2. For comparison, Mg ethylsulphinate, from SO_2 and MgEtBr in Et_2O, is transformed by HCl in light petroleum of low b.p. into ethylsulphinic acid, which with cold $SOCl_2$ affords *ethylsulphinyl chloride*, b.p. 53°/15—16 mm. This with cold EtOH gives *Et ethylsulphinate*, b.p. 60°/13—14 mm., which is not autoxidisable, does not yield Se with SeO_2, and converts $KMnO_4$ into MnO_2 without apparent stoicheiometric relationship. It is hydrolysed to *K ethylsulphinate*. H. W.

Esters of titanium. J. S. JENNINGS, W. WARDLAW, and W. J. R. WAY (J.C.S., 1936, 637—640).—$TiCl_4$ with NaOMe–MeOH or NaOEt–EtOH, but not with the alcohol alone (cf. $SiCl_4$), gives $Ti(OMe)_4$, sublimes at 300°/18 mm., and $Ti(OEt)_4$, b. p. 142°/18 mm. $TiCl_4$ and dry MeOH give *dimethoxydichlorotitanium*, +MeOH, a solid. $Ti(OEt)_4$ and AcCl at 70—80° yield *triethoxychlorotitanium*, anhyd., b.p. 176°/18 mm., and +EtOH, cryst., unaffected by HCl, which with AcCl gives *diethoxydichlorotitanium*, anhyd., b.p. 142°/18 mm., +MeOH and +EtOH, cryst., also obtained from $TiCl_4$ and EtOH at 80—100° and by the method of Demarçay (A., 1875, 441), whose formulation of the compound is erroneous. Similarly are obtained *di*iso*propoxy-*, anhyd., b.p. 160°/18 mm., solid, and $+Pr^{\beta}OH$, cryst., and *di*iso*butoxy-dichlorotitanium*, anhyd., b.p. 184°/18 mm., solid, and +MeOH, +EtOH, and $+Bu^{\beta}OH$ (also obtained from $TiCl_4$ and $Bu^{\beta}OH$ at 100—110°), cryst. R. S. C.

Complex compounds of iridium.—See this vol., 810.

Action of anhydrous ferric chloride on anhydrous acetic and formic acids.—See this vol., 691.

Mechanism of organic reactions. IV. Pyrolysis of esters and acetals. E. M. BILGER and H. HIBBERT (J. Amer. Chem. Soc., 1936, 58, 823—826).—The nos. quoted after the following compounds denote the mols. of olefine and acid, respectively, produced during their decomp. at 470—500°: EtOAc 0·174, 0·176; glycol ethylidene ether 0·023, 0·005; $Pr^{a}CO_2Et$ 0·139, 0·14; Et *n*-butyral (? glycol *n*-butylidene ether) 0·048, 0·029; HCO_2Et 0·122, 0·026; glycol methylene ether 0·008, 0·003; $Pr^{a}OAc$ 0·097, 0·14; propylene acetal 0·021, 0·024; propylene *n*-heptal, b.p. 204°, 0·04, 0·015; trimethylene glycol *n*-butylidene ether 0·04, 0·009; $Bu^{a}OAc$ 0·151, 0·157; $Bu^{\beta}OAc$ 0·141, 0·155; *sec.*-BuOAc 0·177, 0·18; $Pr^{\beta}OAc$ 0·181, 0·181. The cyclic acetals are more stable than the isomeric esters and cannot be intermediates in the decomp. of the latter. Pyrolysis of $CH_2Cl·CH_2·OAc$ and $CH_2Cl·CO_2Et$ gives 38·1% of $CH_2:CHCl$ and 58·2% of C_2H_4, respectively. Decomp. of EtBr (at 482°) and $Bu^{a}Br$ (at 484°) affords 58·7% of C_2H_4 and 41·6% of C_4H_8, respectively. The olefine produced during decomp. of esters arises solely from OAlk. The results are best explained by the intermediate production of free radicals. H. B.

Exchange of hydrogen atoms in the methyl group of heavy acetic acid. A. DADIEU and W. ENGLER (Naturwiss., 1936, 24, 318).—Acetic acid prepared by the action of H_2SO_4 on $(CD_3·CO_2)_2Ba$ gave a Raman line corresponding to a C·H linking. The substitution of D by H may have taken place either through the intermediate formation of $SO_3H·CD_2·CO_2H$ with subsequent hydrolysis, or through an enol form of $CD_3·CO_2H$. W. O. K.

Catalytic preparation of esters of glycol and acetic acid. II. M. B. TUROVA-POLAK and V. F. DZIOMA (J. Appl. Chem. Russ., 1936, 9, 696—702).—$(CH_2·OAc)_2$ (I) is obtained in 70% yield from AcOH and glycol, at 160—170°, in presence of wood-C heated at 200° with an equal wt. of H_3PO_4. Only

traces of $OH{\cdot}CH_2{\cdot}CH_2{\cdot}OAc$ are obtained from 1 : 1 AcOH–glycol mixtures, the chief product being (I).
R. T.

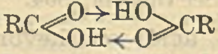
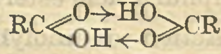
Organic deuterium compounds. Acetic, malonic, and succinic acids. J. O. Halford and L. C. Anderson (J. Amer. Chem. Soc., 1936, 58, 736—740; cf. Wilson, A., 1935, 731).—$CD_2(CO_2D)_2$, m.p. 130—131° [from C_3O_2 and D_2O or by successive crystallisation of $CH_2(CO_2H)_2$ from D_2O], heated at 150° gives $CD_3{\cdot}CO_2D$ (I), m.p. 15·8—16°, converted by dry HCl into trideuteracetic acid (II), $CD_3{\cdot}CO_2H$, m.p. 17·2°. Anhyd. KOAc and conc. D_2SO_4 in D_2O afford acetic deuteracid (III), $CH_3{\cdot}CO_2D$, m.p. 15·4° (cf. Lewis and Schutz, A., 1934, 391). V.p. of (I)—(III) between 21° and 83·6° are recorded. Successive treatment of $(\vdots C{\cdot}CO_2K)_2$ with Na–Hg in D_2O and D_2O–DBr gives tetradeuterosuccinic deuteracid, $({\cdot}CD_2{\cdot}CO_2D)_2$, m.p. 178—179·1°, which when crystallised from D_2O affords tetradeuterosuccinic acid, $({\cdot}CD_2{\cdot}CO_2H)_2$, m.p. 181—182·6°. Succinic deuteracid, $({\cdot}CH_2{\cdot}CO_2D)_2$, m.p. 179—180°, is obtained from succinic acid and D_2O. The relationship between m.p. and D content is discussed. H. B.

Wall effect in the thermal polymerisation of unsaturated esters. J. W. Breitenbach and R. Raff (Ber., 1936, 69, [*B*], 1107—1110).—Polymerisation of Me acrylate and vinyl acetate occurs fairly rapidly, but quite irregularly, when they are heated in glass vessels, and is greatly influenced by the nature and pre-treatment of the glass. In pure Ni vessels only slight polymerisation is observed after several days at 100°; it is readily induced by powdered glass and, particularly, by Na_2SiO_3. Similar differences are not observed with styrene. The phenomena are attributed to the alkali of the glass towards which esters, but not hydrocarbons, are very sensitive.
H. W.

Electrolysis of mixtures of *n*-butyrates with nitrates. F. Fichter and F. Metz (Helv. Chim. Acta, 1936, 19, 597—606).—By electrolysing a mixture of $4N$-$PrCO_2Na$ and $2N$-$NaNO_3$ at 18—20° with a c.d. of 0·166 amp. per sq. cm. an oil was obtained comparable with that from the corresponding propionate electrolysis (A., 1935, 472). It contained $Pr^{a}NO_2$, n-C_6H_{14}, $Pr^{\beta}NO_3$, $Pr^{a}CO_2Pr^{\beta}$, $CHMeBu^{a}{\cdot}O{\cdot}NO_2$, $CHMePr^{\beta}{\cdot}O{\cdot}NO_2$, $NO_3{\cdot}CHMe{\cdot}CH_2{\cdot}NO_3$, $NO_3{\cdot}CMe_2{\cdot}[CH_2]_3{\cdot}NO_3$, and glyceryl esters. The results are discussed with reference to previous observations (cf. *loc. cit.*; A., 1935, 730, 1105). M. S. B.

Catalytic hydrogenation of sorbic acid.—See this vol., 808.

Hydrogenation of Δ^9-octadecenyl Δ^9-octadecenoate (oleyl oleate). T. P. Hilditch and H. Paul (J.C.S., 1936, 664—667).—Hydrogenation (Ni–kieselguhr) of oleyl oleate at 180° is largely non-selective, but there is slight preferential reaction of the oleyl ethylenic linking and slightly more formation of $C_{17}H_{35}{\cdot}CO_2{\cdot}C_{18}H_{37}$ (I) than is calc. from probability data. The proportions of the products in the reaction mixture after varying times of hydrogenation are determined by the I val., oxidation by $KMnO_4$ and isolation of unattacked (I), followed by hydrolysis and isolation of the $C_{18}H_{37}{\cdot}OH$. Other oxidation products could not be isolated quantitatively. R. S. C.

Higher aliphatic compounds. VI. Existence of compounds in binary systems from palmitic, margaric, stearic, tricosanoic, and tetracosanoic acids. J. C. Smith (J.C.S., 1936, 625–627; cf. A., 1933, 1271).—Mixed m.-p. diagrams of the pure acids indicate formation of 1 : 1 compounds of tricosanoic with tetracosanoic, palmitic (I) with margaric (II), stearic (III) with (II), and palmitic with stearic acid, with formation of complete solid solutions. Liquidus curves show the possibility also of compounds, 3(II) : 1(I), 3(II) : 1(III), and 1(II) : 3(III). Previous reports that acids with an odd no. of C do not form compounds with acids with an even no. of C were due to use of impure acids. It is suggested that the 3 : 1 compounds may be due to alternate layers of  $\mathrm{RC}{<}\begin{matrix}\mathrm{O}\rightarrow\mathrm{HO}\\ \mathrm{OH}\leftarrow\mathrm{O}\end{matrix}{>}\mathrm{CR}$ and  $\mathrm{RC}{<}\begin{matrix}\mathrm{O}\rightarrow\mathrm{HO}\\ \mathrm{OH}\leftarrow\mathrm{O}\end{matrix}{>}\mathrm{CR'}$.
R. S. C.

Soap solutions. XI. Reactions between the systems: stearic acid–sodium oleate and oleic acid–sodium stearate. J. Mikumo (J. Soc. Chem. Ind. Japan, 1936, 39, 98—100B).—The reactions have been studied in MeOH, EtOH, and MeOH–C_6H_6 mixtures. The *compound* $C_{18}H_{35}O_2Na,C_{18}H_{36}O_2$, m.p. 119—120°, is produced in each case and its crystallographic properties are described. R. S.

Lipins of wheat embryo. I, II.—See this vol., 912.

Naming of the highly unsaturated acid of the kernel fat of "akarittom," *Parinarium laurinum*. M. Tsujimoto (J. Soc. Chem. Ind. Japan, 1936, 39, 116—117B).—The name *parinaric acid* (I) is suggested for the unsaturated acid $C_{18}H_{28}O_2$ (Farmer *et al.*, A., 1935, 1041) isolated from the kernel fat of *P. laurinum* (B., 1933, 476). (I) is not identical with couepic acid. J. W. B.

Determination of hydroxyl number of hydroxy fatty acids. K. Hinsberg (Biochem. Z., 1936, 285, 125—129).—The acid (0·6 g. of dihydroxystearic acid) is acetylated with a known amount of dry C_5H_5N–Ac_2O and an aliquot of the reaction product distilled in vac. in a described apparatus, the Ac_2O remaining and the AcOH formed being absorbed in standard KOH and the OH val. being calc. by difference. P. W. C.

Optical properties of fermentation lactic acid. III.—See this vol., 899.

M.-p. curves of optical isomerides. J. D. M. Ross (J.C.S., 1936, 718—723).—Mixed setting-point curves of the *d*- and *l*-forms of $CCl_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2R$ (I; R=H. II; R=Me) and $OH{\cdot}CHPh{\cdot}CO_2R$ (III; R=Me or Et) show formation of the racemate in all cases. Kremann's method shows dissociation of the racemates as follows: (I) 10, (II) 16, (III) 20%; van Laar's method gives erroneous results. $OH{\cdot}CHPh{\cdot}CO_2H$ decomposes slightly at the m.p.
R. S. C.

Behaviour of lævulyl chloride and acetyllævulic acid in the Friedel–Crafts reaction. J. H. Helberger (Annalen, 1936, 522, 269—277).—Lævulyl chloride (I) (1 mol.) (from the acid and $SOCl_2$), C_6H_6 (excess), and $AlCl_3$ (1 mol.) at 50° give 58% of phenacylacetone (II), b.p. 158°/12 mm., m.p. 28—29°, and some of the diphenylvaleric acid (III), m.p. 116—118°, of Eykman (A., 1908, i, 22); in presence of $PhNO_2$, about the same amount of (III) but little (II) result. The formation of (II) shows that (I) can react as $CH_2Ac·CH_2·COCl$. Acetyllævulic acid [γ-acetoxy-γ-valerolactone], C_6H_6, and $AlCl_3$ (3 mols.) at 45—50° afford (II) (60%), (III) (trace), and a little COPhMe; with PhMe and PhOMe, p-*methyl-*, b.p. 168°/12 mm., m.p. 53°, and p-*methoxyphenacylacetone*, respectively, are formed. NH_2Ph and (II) with a little AcOH at 100° give 1 : 5-diphenyl-2-methylpyrrole, m.p. 83°; *p*-$NO_2·C_6H_4·NH_2$ similarly affords a *pyrrole*, $C_{17}H_{14}O_2N_2$, m.p. 103°; *o*-$NH_2·C_6H_4·CO_2H$ yields a *pyrrole*, $C_{18}H_{15}O_2N$, m.p. 184° (becoming red); *p*-$C_6H_4(NH_2)_2$ furnishes *pyrroles*, $C_{17}H_{16}N_2$, m.p. 137°, and $C_{28}H_{24}N_2$, m.p. 230° [from 1 and 2 mols. of (II), respectively]; benzidine gives a *pyrrole*, $C_{34}H_{28}N_2$, m.p. 229°.

H. B.

Raman spectrum of oxalic acid.—See this vol., 777.

Detection of oxalate ion by decolorisation of indigotin solution according to Tananaev and Budkevitsch. A. S. Komarovski and V. A. Nasarenko (Z. anal. Chem., 1936, **104**, 413—416; cf. this vol., 190).—The reaction is not sp. Other org. acids, NO_2', and small amounts of Fe''' produce the same effect, whilst Mo, W, or Zr inhibit the action by complex formation.

J. S. A.

Tetradeuterosuccinic acid and derivatives. A. McLean and R. Adams (J. Amer. Chem. Soc., 1936, **58**, 804—810).—$(:C·CO_2Me)_2$ is reduced (D_2, PtO_2, EtOAc) to *Me tetradeuterosuccinate*, b.p. 195·3°/743 mm., m.p. 17°, hydrolysed (very dil. HNO_3) to *tetradeuterosuccinic acid*, m.p. 180—180·5° (*anhydride*, m.p. 119·3—119·6°). Other physical data are given. Reduction occurs more slowly with D_2 than with H_2. Apparatus for (i) the production of D_2, (ii) reduction, and (iii) determination of *d* for solids which melt without decomp., is described.

H. B.

Mol. wts. of polymeric substances in pyrocatechol and their bearing on the nature of coal and derived products. R. C. Smith and H. C. Howard (J. Amer. Chem. Soc., 1936, **58**, 740—742).—Mol. wt. determinations (f.-p. method) of various polymeric substances (*e.g.*, C_2H_4 succinate, adipic anhydride, lactide, tetraethylene glycol, synthetic resins) in *o*-$C_6H_4(OH)_2$ and Ph_2 (when sol.) indicate that (except when chemical degradation occurs) the anomalous behaviour exhibited by the products derived from coal (B., 1935, 534) is generally absent. The latter products must be built up of relatively small units.

H. B.

Constitution of the reduction product of trichloromethylparaconic acid. A. N. Meldrum and R. D. Kotwal (J. Indian Chem. Soc., 1936, **13**, 213—216).—The reduction product of trichloromethylparaconic acid (*Me₂*, m.p. 77°, *Et₂*, b.p. 173°/10 mm., and *Et H* esters, b.p. 190°/20 mm.; *anilide*, m.p. 165—166°; p-*toluidide*, m.p. 173—174°; *anilic acid*, m.p. 121—122°) is not  $O\!<\!\begin{matrix}CO—CH_2\\CH(CCl_3)\end{matrix}\!>\!CH·CO_2H$ (Fittig *et al.*, A., 1888, 251) but is δδ-*dichloro*-n-*butane*-αβ-*dicarboxylic acid* [*Me₂*, b.p. 135°/11 mm., and *Et₂*, b.p. 215°/50 mm., esters; *anhydride*, m.p. 76—77°; *acid chloride*, b.p. 123°/5 mm. (not pure); *dianilide*, m.p. 176—177°; *di*-p-*toluidide*, m.p. 209—210°], converted by conc. H_2SO_4 at 100° into tricarballylic acid.

J. W. B.

Active methyldiglycollic acid and its derivatives. M. Godchot and P. Vièles (Compt. rend., 1936, **202**, 1358—1360).—*d*-Lactic acid (1 mol.), anhyd. $CuSO_4$ (1 mol.), and the alcohol (4 mols.) when heated for 16 hr. give the Me, b.p. 49°/20 mm., $[\alpha]^{20}$ +9·51°, and Et esters, b.p. 58°/20 mm., $[\alpha]^{20}$ +12°. These with $CH_2Cl·CO_2R$ give *methyldiglycollic* [α-*carbalkoxymethoxypropionic*] esters, in which (*a*) R=R′=Me, b.p. 118°/20 mm., $[\alpha]^{20}$ −4·47°, and Et (I), b.p. 127°/20 mm., $[\alpha]^{20}$ −9·77°, (*b*) R=Me, R′=Et, b.p. 124°/20 mm., $[\alpha]^{20}$ −2·07°, and (*c*) R=Et, R′=Me, b.p. 125°/20 mm.; $[\alpha]^{20}$ −11·96°. Hydrolysis of (I) by NaOH–EtOH gives the l-*acid*, m.p. 70°, $[\alpha]^{20}$ −6·71° in Et_2O, which with hot Ac_2O gives the *anhydride*, b.p. 118°/17 mm., $[\alpha]^{20}$ −2° in Et_2O, easily hydrolysed to the active acid.

R. S. C.

Constitution of some tartaric complexes and their physico-chemical applications. I. Tungsto-, II. Molybdo-, III. Boro-, IV. Alumino-, V. Antimonio-tartaric complexes. T. K. Heng (J. Chim. phys., 1936, **33**, 356—377, 377—383, 383—403, 403—413).—A polarimetric study has been made of the complexes formed by some compounds of W, B, Mo, Al, and Sb with tartaric acid (=H_2T), tartramic acid (=HNH_2T), tartramide [=$(NH_2)_2T$] in aq. solution, in order to determine which parts of the H_2T mol. are involved in each case.

I. (Cf. Gernez, A., 1888, 938; Grossmann and Pötter, A., 1906, ii, 211; Henderson and Barr, J.C.S., 1896, **69**, 1451). H_2WO_4 gives with H_2T, $H_2WO_4,2H_2T$ (I), and with HNH_2T, $H_2WO_4,2HNH_2T$, hence only 1 CO_2H of each H_2T mol. in (I) is fixed. $NaHWO_4$ gives with H_2T $[H_2T,2WO_3]Na_2$, and with HNH_2T, $[HNH_2T,2WO_3]Na_2$. Na_2WO_4 gives with H_2T,$[H_2T,WO_3]Na_2$ (II); with NaHT, $(2H_2T,WO_3)Na_4$ (III); with HNH_2T, $[HNH_2T,2WO_3]Na_2$; with $NaNH_2T$, no compound, indicating that in (II), both CO_2H of the H_2T mol. are fixed. (III) can be obtained cryst. in very small quantity. With malic acid (=H_2M), H_2WO_4 gives $H_2WO_4,2H_2M$; $NaHWO_4$ gives $[H_2M,2WO_3]Na_2$ (cryst. powder hydrated); Na_2WO_4 gives $[2H_2M,WO_3]Na_2$, (very easily cryst., α_J^{20} −34·5°). No compound $[H_2M,WO_3]Na_2$ exists.

II. (Cf. Gernez, A., 1887, 540; Rosenheim and Itzig, A., 1900, i, 272; Grossmann and Pötter, *loc. cit.*). H_2MoO_4 gives with H_2T, $2H_2T,H_2MoO_4$, but with HNH_2T, HNH_2T,H_2MoO_4. $NaHMoO_4$ gives with H_2T, $[H_2T,2MoO_3]Na_2$ (IV); with NaHT, $[2H_2T,MoO_3]Na_4$ (V). Na_2MoO_4 and H_2T give $[H_2T,MoO_3]Na_2$ (VI). Corresponding with these three Na compounds with H_2T, only one, $[2HNH_2T,MoO_3]Na_2$ (VII), with HNH_2T exists. Structural formulæ for (IV)—(VII) are advanced.

III. (Cf. Darmois, A., 1926, 351, 457; 1930, 854; Lowry, J.C.S., 1929, 2853; Jones, J.C.S., 1933, 952). Gradual addition of KBO_2 to H_2T gives at first H_2T,KBO_2, and later BTK_2; finally (considerable excess of KBO_2) BTK. The complex $2H_2T,KBO_2$ (or BT_2K) described by Lowry does not exist in aq. solution. Me_2T gives with KBO_2, at first Me_2T,BO_2K, but after 2 months H_2T,KBO_2, and not $2H_2T,KBO_2$, as found by Darmois (A., 1927, 448) by hydrolysis of Et_2T with KBO_2. $NaBO_2$ gives with $(NH_2)_2T$, $(NH_2)_2T,NaBO_2$, $\alpha_J^{20}+69{\cdot}5°$, analogous to the spirans, and with HNH_2T, $2NH_2HT,NaBO_2$.

IV. (Cf. Quadrat and Korecky, A., 1909, i, 762). $Al(OH)_3$ dissolves in aq. H_2T to give $H_2T,Al(OH)_3$ which is lævorotatory in conc., and dextrorotatory in dil., solution. HNH_2T gives $HNH_2T,Al(OH)_3$, which is lævorotatory in all concns. $(NH_2)_2T$ gives no compound. Addition of NaOH to a mixture of Na_2T and $Al_2(SO_4)_3$ gives a very basic solution of $(AlT_3)Na_3$, from which Al cannot be pptd. by Na_2HPO_4. The mechanism of formation of this compound is discussed. $(AlT_3)K_3$ can be obtained by hydrolysis of Me_2T with $KAlO_2$. From these results a polarimetric method of studying the corrosion of Al by NaOH is suggested.

V. (Cf. Darmois, A., 1927, 448). A mixture of SbF_3 and H_2T when gradually neutralised gives a ppt. of tartar emetic at the correct concn. Similar compounds are obtained when H_2T is replaced by any of its salts, inorg. or org. Since aq. SbF_3 attacks glass (by hydrolysis), a polarimetric method of studying the corrosion of glass by HF is indicated and developed. R. C. M.

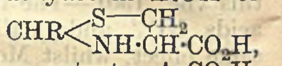
Determination of citric acid by conversion into acetone. II. K. Täufel and K. Schoierer (Z. Unters. Lebensm., 1936, **71**, 297—310; cf. A., 1933, 807).—Citric acid is pptd. by aq. $Bi(NO_3)_3$–mannitol, and oxidised either with $KMnO_4$ to $COMe_2$, which is determined by the CHI_3 method, or with $Fe_2(SO_4)_3$ in presence of light to acetonedicarboxylic acid, which is determined by pptn. with Denigès' $HgSO_4$ reagent. An improved procedure is described for the removal of substances which interfere in the former method. E. C. S.

Polarimetric study of the formation of complex molybdosaccharates.—See this vol., 691.

Synthesis of aldobionic acid of gum acacia. R. D. Hotchkiss and W. F. Goebel (J. Amer. Chem. Soc., 1936, **58**, 858—859).—Me acetobromoglycuronate (A., 1935, 1483), 1 : 2 : 3 : 4-di*iso*propylidenegalactose, and Ag_2O in Et_2O give 1 : 2 : 3 : 4-*diisopropylidenegalactose*-6-β-*triacetylglycuronide Me* ester, m.p. 112·5—114°, $[\alpha]_D^{25}$ −68° in $CHCl_3$, hydrolysed [first $Ba(OH)_2$ then dil. H_2SO_4] to galactopyranose-6-β-glycuronopyranoside (I), which is identical with the aldobionic acid (II) from gum acacia (Heidelberger and Kendall, A., 1930, 66; cf. Challinor *et al.*, A., 1931, 465). (I) and (II) with CH_2N_2 give the same *Me* ester, m.p. 119° (decomp.), $[\alpha]_D$ (in H_2O) $-2{\cdot}9° \rightarrow -9{\cdot}1°$ (*Ac*$_7$ derivative, m.p. 202—203°, $[\alpha]_D^{25}$ −17·5° in $CHCl_3$). H. B.

Synthesis of the hepta-acetyl methyl ester of gentiobiuronic acid. R. D. Hotchkiss and W. F. Goebel (Science, 1936, **83**, 353—354).—Condensation of β-glucose 1 : 2 : 3 : 4-tetra-acetate, with Me 1-bromotriacetylglycuronate in $CHCl_3$ in presence of Ag_2O yields the β-hepta-acetyl Me ester (I) of the aldobionic acid, glucose-6-β-glycuronide. (I), m.p. 198—199° has $[\alpha]_D^{23}$ −11·0 in $CHCl_3$, and is converted into the α-isomeride, m.p. 201—202°, $[\alpha]_D^{23}$ +48·4° in $CHCl_3$, by the action of $ZnCl_2$ in Ac_2O. L. S. T.

Disulphoacetic acid. H. J. Backer and N. Benninga (Rec. trav. chim., 1936, **55**, 370—373).—Oxidation of $CH(SO_3H)_2{\cdot}CHO$ with either AcO_2H–aq. H_2O_2 at 50° or Ag_2O on a water-bath affords *disulphoacetic acid* +2·5 H_2O, sinters 78°, m.p. 85—86°, isolated as its *Ag*$_3$+H_2O salt (*Ba*+9H_2O, *K*+H_2O, *NH$_2$Ph*, *strychnine* +8H_2O, and *quinine* +5H_2O salts). When heated at 110—130° it decomposes into CO_2 and $CH_2(SO_3H)_2$. J. W. B.

Compounds of thiol-acids with aldehydes. M. P. Schubert (J. Biol. Chem., 1936, **114**, 341—350).—Aldehydes, RCHO, and $SH{\cdot}CH_2{\cdot}CO{\cdot}NHPh$ (I) in EtOH give α′-*hydroxyalkylthiolglycolanilides* (II), $OH{\cdot}CHR{\cdot}S{\cdot}CH_2{\cdot}CO{\cdot}NHPh$, which, although they can be recrystallised, are more or less dissociated in solution, but give rather more stable Ac derivatives. $AcCO_2H$, benzoquinone, and isatin give similar compounds, but $COMe_2$, COPhMe, Ac_2, and Bz_2 do not. Cysteine and aldehydes in EtOH or H_2O give thiazole derivatives,  $CHR{<}\genfrac{}{}{0pt}{}{S\text{——}CH_2}{NH{\cdot}CH{\cdot}CO_2H}$, which dissociate to a smaller extent; $AcCO_2H$, however, gives (β-*lactic acid*)*thiolalanine*, $CO_2H{\cdot}CMe(OH){\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$ (III), which is of type (II). The following derivatives of (II) are described, in which R=H, m.p. 91—92° (*Ac* derivative, m.p. 91—92°), Pr, m.p. 73—75°, CCl_3, m.p. 111—112° (*Ac* derivative, m.p. 133—134°), and *compounds*, $OH{\cdot}CR{\cdot}S{\cdot}CH_2{\cdot}CO{\cdot}NHPh$, in which R is a residue from benzoquinone, m.p. 165—166°, and isatin, m.p. 101°, and (β-*lactic acid*)*thiolacetanilide* (from $AcCO_2H$), m.p. 90—92°. These OH-compounds give a colour with Na nitroprusside (IV) in aq. $NaHCO_3$ [although less strongly than does (I)] and can be titrated with I [1 atom consumed to give $({\cdot}S{\cdot}CH_2{\cdot}CO{\cdot}NHPh)_2$]; the Ac derivatives consume I only very slowly and give no colour with (IV). (I) reacts with the compound (V) from $CHO{\cdot}COPh$ and $SH{\cdot}CH_2{\cdot}CO_2H$ to ppt. the less sol. *hydroxybenzoylmethylthiolacetanilide*, $COPh{\cdot}CH(OH){\cdot}S{\cdot}CH_2{\cdot}CO{\cdot}NHPh$, m.p. 148°. 4-*Carboxytetrahydrothiazole*, m.p. 195° (decomp.), and its 2-*CCl*$_3$ (VI), cryst., -*Pr* (VII), m.p. 167—168°, -*Ph* (VIII), m.p. 159—160° (*Ac* derivative, m.p. 202°), and -2′-*furyl* (IX) derivative, m.p. 125—126°, are described; they liberate CO_2 from $NaHCO_3$ and dissolve in aq. NaOAc. Only (VI) gives a colour with (IV) in aq. $NaHCO_3$, but in dil. aq. NH_3 (VI), (VII), and (IX) give the test strongly and (VII) weakly. Even if the test is negative, some dissociation occurs, since in $NaHCO_3$ (VIII) and $CH_2I{\cdot}CO_2Na$ produce PhCHO and $CO_2H{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$, and $CHPh{:}N{\cdot}NHPh$ is obtained from (VIII) and $NH_2{\cdot}NHPh$ in 2*M*-aq. KOAc. The thiazoles, but not the Ac derivative, absorb I readily to give cystine. (III), m.p. 150—151°, but not its *Ac*$_2$ derivative (prep. by AcOH–C_5H_5N), m.p. 201—202° (decomp.), can be titrated with I; neither gives a colour with

(IV), even in dil. aq. NH_3. (I) and (V) give *Ac* derivatives, m.p. 91° and 202°, respectively. R. S. C.

Preparation of carboxylic acids of organic selenides. A. Fredga (Svensk Kem. Tidskr., 1936, **48**, 91—98).—Selenolcarboxylic acids $SeR{\cdot}CH_2{\cdot}CO_2H$ are prepared by interaction (air excluded) of $Hg(Se{\cdot}CH_2{\cdot}CO_2Na)_2$ and Na_2S in H_2O to give $SeNa{\cdot}CH_2{\cdot}CO_2Na$, and treatment of the resulting solution with the alkyl halide in MeOH or EtOH. Thus from the appropriate halide are obtained *benzyl-*, m.p. 71—72° (*Cu* salt), *methylenebis-*, m.p. 122·5—123° (*Cu* salt), *ethane-αβ-di-*, m.p. 153—154° (only 2% yield, much C_2H_4 formed) (*Cu* salt), and *propane-αγ-di-selenolacetic acid*, m.p. 77—78° (*Cu* salt). Similarly from $Hg(Se{\cdot}[CH_2]_2{\cdot}CO_2H)_2$ are prepared β-*benzylselenolpropionic acid*, m.p. 75—76° (*Cu* salt), and β-*carboxymethylselenolpropionic acid*, m.p. 91—92°. J. W. B.

Slow combustion of formaldehyde.—See this vol., 801.

Reaction of formaldehyde with hydrogen peroxide in heavy water.—See this vol., 688.

Thermal decomposition of acetaldehyde and ethylene oxide: existence of short-lived intermediates. M. W. Travers and R. V. Seddon (Nature, 1936, **137**, 906—907).—The rates of decomp. are accelerated initially, the acceleration being more marked in the case of $(CH_2)_2O$, which exhibits an induction period. The processes involved are evidently more complex than hitherto supposed. With MeCHO at 360—500° over a wide range of concn., decomp. follows alternative courses either into (i) CH_4 and CO or (ii) propylene and CO. (i) is dominant in unpacked and (ii) in packed tubes. Some propylene is always formed in (i) and it undergoes some condensation to produce a 6-carbon hydrocarbon and more complex products. Although packing retards (i) and accelerates (ii) the total rate of decomp. is independent of the nature or dimensions of the reaction tube. The formation of a short-lived intermediate is probable. L. S. T.

Electrolytic reduction of aliphatic ketones.—See this vol., 687.

Action of bromine on acetone in presence of various solvents. T. Tomonari (Z. physikal. Chem., 1936, **B**, **32**, 222—228).—The bromination is retarded by H_2O and to a smaller extent by alcohols, the effect falling and ultimately changing in sign with increasing chain length. This phenomenon is ascribed to the $COMe_2$–H_2O or $COMe_2$–alcohol complex retarding the enolisation of the $COMe_2$. In $COMe_2$–CS_2 and $COMe_2$–C_6H_{14} mixtures and in pure $COMe_2$ the rate is determined primarily by the amount of catalyst. R. C.

Metal ketyls of the aliphatic series. IV. Action of sodium on *tert.*-butyl *tert.*-amyl and on *tert.*-butyl *tert.*-hexyl ketones. I. N. Nazarov (Compt. rend. Acad. Sci. U.R.S.S., 1936, **2**, 71—75).—$COBu^{\gamma}{\cdot}CMe_2Et$ (I) (from $COPr^{\beta}Bu^{\gamma}$, $NaNH_2$, and EtI) in Et_2O with Na for 26 days affords (I) and tert.-*butyl*-tert.-*amylcarbinol* (II), b.p. 186—190°. From the above reaction mixture and EtI, (I), (II), and $NH_2{\cdot}CO_2Ph$ are obtained. Using BzBr instead of EtI the main product is *benzoyl*-tert.-*butyl*-tert.-*amylcarbinol*, b.p. 182—186°/22 mm., partly converted by 6*N*-KOH–EtOH during 7 hr. into (II). Reaction between $COBu^{\gamma}{\cdot}CMeEt_2$ (III) (from $COBu^{\gamma}{\cdot}CHEt_2$, $NaNH_2$, and MeI) and Na in Et_2O was incomplete after 4 months. Decomp. of the reaction mixture affords (III) and tert.-*butyl*-tert.-*hexylcarbinol* (IV), b.p. 190—208° (*phenylurethane*, m.p. 97—98°). (III) and (IV) are also obtained from the above reaction mixture and EtI. P. G. C.

Crystalline constituent of essential oil of matsubasa.—See this vol., 651.

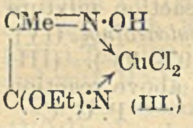
Diacetyl. J. Pien, J. Baisse, and R. Martin (Ann. Falsif., 1936, **29**, 204—225).—The prep. of Ac_2 from CMeEt:N·OH, its recognition by formation of the yellowish-brown xyloquinone, and the characterisation by means of the phenylhydrazone and particularly by its reaction with 3 : 4-tolylenediamine and H_2SO_4 are described. The yellow colour of the quinoxaline is appreciable at dilutions of 1 : 100,000 and for the determination, $K_2Cr_2O_7$ solutions may be used as colour standards. Conversion into the dioxime and treatment with a Ni salt is not sensitive. The formation of Ac_2 in milk products and its isolation and determination are discussed. E. H. S.

Cobalt salts of glyoximes. I. II. Diglyoxime and sesquiglyoxime cobaltic salts. L. Cambi and (Signa.) C. Coriselli (Gazzetta, 1936, **66**, 81—91, 91—99).—I. The red series of complex Co derivatives of glyoximes represents Co^{II}, whilst the green series (A., 1924, i, 20) represents Co^{III}, Co^{II} salts being very readily oxidised in presence of glyoximes. The magnetic susceptibilities (χ) at 84—294° abs. of a no. of complexes are tabulated. In simple additive compounds of the type $(DH_2)_2Co^{II}X_2$ (DH_2 = $OH{\cdot}N{:}CMe{\cdot}CMe{:}N{\cdot}OH$), χ is additive; salts of the red series (A., 1931, 938) belong to this type. Those of the green series are diamagnetic, and thus have the structure $[(DH)(DH_2)Co^{III}X_2]$ or $[(DH_2)_2Co^{III}X_2]H$; they are obtained in EtOH from CoX_2 and (DH_2), in presence of acid and of O_2. With $NH(CH_2Ph)_2$, and of other *sec.* amines, $[(DH)(NH_2)CoBr_2]$ (I) forms *salts* of type $[(DH)_2CoBr_2]NH_2(CH_2Ph)_2$, which are reconverted into (I) by HBr. With NH_3, the *complex* $[(DH)_2Co(NH_3)_2]Br$ is formed, or, using NH_4OAc, $[(DH)_2Co(NH_3)Br]$. With $AgNO_2$ and NaOAc, (I) yields the *complex* $[(DH)_2Co(NO_2)_2]Na,H_2O$, in which Na can be replaced by the ion $NH_2Bu^{\beta}{}_2$, or by H. With KOH, (I) gives the *salt* $[(DH)_2Co(OH)_2]K$. Action of KOAc on (I) yields the diamagnetic *complexes* $[(DH)_2Co(OH)]$ and $[(DH)Co(D)]$, which are reconverted into (I) by HBr.

II. $Co(OAc)_2$+AcOH and DH_2 in boiling EtOH absorb O_2 to form the complex $[Co_2(D)_3]$ (II), also obtained from $[(DH)Co(D)]$ and DH_2, or from Co and DH_2; (II) with HBr yields $[(DH)(DH_2)CoBr_2]$. The p-*tolylmethyl-* and *diphenyl-glyoxime* analogues of (II) behave similarly. χ of (II) varies according to method of prep. The structures of $[(DH)Co(D)]$ and of (II) are discussed. E. W. W.

Methylalkoxyglyoximes as chelate groups. E. Sharratt and W. Wardlaw (J.C.S., 1936, 563—

567).—When OH·N:CH·CMe:N·OH (I) (*Ni* derivative, decomp. 243°) and $CuCl_2$ react in EtOH and the complex (I) produced (this vol., 410) is removed, the filtrate slowly deposits *Cu methylethoxyglyoxime dichloride* (III), m.p. 165° (decomp.), decomposed by H_2O, $\kappa=3{\cdot}471\times10^{-5}$ at 25°; it is produced from (II) and EtOH by oxidation and its structure is proved by the following reactions. (III) is not obtained from (II) in the absence of air, with aq. Na_2S gives *methylethoxyglyoxime* (IV), m.p. 142° (*Ni* derivative, m.p. 197°), and with H_2S–aq. EtOH gives OH·N:CHMe·CO_2Et, m.p. 95° [produced from (IV) by the HCl liberated; modified prep.]. (I) and $CuCl_2$ in MeOH do not ppt. a complex analogous to (II), but slowly yield *Cu methylmethoxyglyoxime dichloride* (V), m.p. 176° (decomp.), which with Na_2S and H_2S gives *methylmethoxyglyoxime*, m.p. 148° (*Ni* derivative, m.p. 223°, decomp. 285°), and OH·N:CHMe·CO_2Me, m.p. 71° (lit. 69°), respectively. When heated in EtOH or MeOH in air, (II) gives (III) and (V), respectively. Dimethyl-, methylethyl- (*Ni* derivative, decomp. 260°), and benzylmethyl-glyoxime yield no such compounds, since they do not possess an oxidisable H. R. S. C.



(III.)

Harding sugar reagent. E. J. King, G. A. D. Haslewood, and G. A. Grant (Nature, 1936, 137, 872).—The Harding–Downs factor for glucose (A., 1933, 964) can be consistently reproduced when reagents of a sufficiently high grade are used. Van der Plank's results (this vol., 650) may be due to the use of inferior reagents. L. S. T.

Enolisation of sugars under the action of different bases. A. Kusin (Ber., 1963, 69, [*B*], 1041—1049).—Solutions of glucose (I) and $Ca(OH)_2$ when acidified after 1 hr. at 30° immediately decolorise dichloroindophenol and absorb I from acid solution, thus showing the presence of enolic OH. In similar circumstances solutions of (I) and NaOH or NaOH–Na_2HPO_4 (p_H 12) have no reducing properties in acid solution. The existence of enolic OH is further established by the rapid disappearance of the reducing action and a fugitive coloration with $FeCl_3$. After 24 hr. at room temp. mannose (II) is present in appreciable amount in solution of (I) and $Ca(OH)_2$, whereas after 48 hr. fructose (III) can scarcely be detected. In solutions of (I) and NaOH (III) can be isolated as Ca fructosate after 24 hr., whereas (II) is present only in traces. It is considered that the enolic form is produced from (I) by $Ca(OH)_2$ without rupture of the pyranose ring, whereas the much less stable enol formed by the action of NaOH has the open-chain structure. H. W.

Optical rotation of *l*-threose. V. Deulofeu (J. Amer. Chem. Soc., 1936, 58, 855; cf. Hockett, this vol., 191).—*d*-Threosediacetamide triacetate, prepared by the method (A., 1933, 147) used for the *l*-erythreose derivative, has m.p. 176—177° $[\alpha]_D$ +38° in H_2O. The compounds of the *l*-threose series (A., 1930, 68) need correction for sign and vals. H. B.

Monomethylhexoses. II. Revision of the constitutions of the supposed 4-methylgalactose and 4-methylmannose of Pacsu, and their formulation as 6-methylgalactose and 2-methylmannose, respectively. J. Munro and E. G. V. Percival (J.C.S., 1936, 640—644; cf. A., 1935, 1108).—The so-called 4-methylgalactose of Pacsu and Lōb (A., 1930, 197) is 6-methylgalactose (I). The experiments of Pacsu and von Kary (A., 1930, 70) on the methylation of di*iso*propylidenemannose-dibenzylmercaptal (II) could not be repeated; the supposed 4-methylmannose was probably 2-methylmannose (III) mixed with mannose and some polymethylated derivatives. (I) was recognised by (*a*) comparison with authentic specimens of the sugar, m.p. 122—123°, $[\alpha]_D^{20}$ +112° (4 min.) → +66° in 6 hr. in H_2O, its phenylosazone, m.p. 200—201°, $[\alpha]_D^{20}$ +144° in C_5H_5N, and phenylhydrazone, m.p. 179°, $[\alpha]_D^{20}$ +24° → +14·8° in 24 hr. in C_5H_5N, (*b*) formation of the Ac_4 derivative, triacetylmethylgalactosidyl bromide, methyltriacetylmethylgalactoside, reaction with Me_2SO_4–NaOH–aq. $COMe_2$ and then with MeI–Ag_2O, and finally hydrolysis by 8% HCl at 100° to 2 : 3 : 4 : 6-tetramethylgalactose, (*c*) oxidation by Br at 35° to a γ-lactone, and (*d*) formation of a mixture of methyl-furanoside and -pyranoside with 0·5% HCl–MeOH. (II), when heated, gives mannosedibenzylmercaptal, $[\alpha]_D^{20}$ +79° in $(CHCl_2)_2$. Pacsu and von Kary's conditions of methylation gave a syrup, yielding a mixture (OMe 2·4%), m.p. 118° (sharp), $[\alpha]_D^{20}$ −48° in C_5H_5N; with $HgCl_2$ the syrup gave only an oil (IV), which afforded a mixture (OMe 11·1%) of methyl-tetra-acetyl- and -triacetyl-methyl-mannosides. More drastic methylation gives products with higher OMe contents which are, however, always mixtures. These syrups all give mannosephenylhydrazone ($\nless$20%) and after removal thereof glucosazone (which must owe its formation to the presence of 2-methylmannose) and small amounts of methylated by-products. The structures of Pacsu's glucose-, galactose-, and mannose-dibenzylmercaptals need revision. R. S. C.

Syntheses with 5 : 6-anhydro*iso*propylideneglucose; *d*-glucosyl-6-phthalimide. H. Ohle and E. Euler (Ber., 1936, 69, [*B*], 1022—1026; cf. this vol., 192).—5 : 6-Anhydro*iso*propylideneglucose and pure *o*-$C_6H_4(CO)_2NH$ do not interact at 140—150°, but in presence of a suitable catalyst, notably C_5H_5N, iso*propylidene*-d-*glucosyl*-6-*phthalimide* (I), m.p. 174°, $[\alpha]_D$ +14·38° in $COMe_2$, is formed in 80% yield. The constitution of (I) follows from its conversion by $COMe_2$ containing $CuSO_4$ and H_2SO_4 into iso*di*iso*propylidene*-d-*glucosyl*-6-*phthalimide*, m.p. 124·5—125·5°, $[\alpha]_D^{19}$ +18·92° in $CHCl_3$, also obtained from *iso*di*iso*propylideneglucose 6-*p*-toluenesulphonate through iso*di*iso*propylidene*-d-*glucosyl*-6-*amine*, b.p. 120° (bath)/0·08 mm., $[\alpha]_D^{19}$ +39·9° in $CHCl_3$. The NH_2 in the *iso*propylideneglucosylamine of Ohle *et al.* (A., 1928, 870) is shown to occupy position 6, since the compound is converted by *o*-$C_6H_4(COCl)_2$ into a non-homogeneous product transformed by alkaline hydrolysis into iso*propylidene*-d-*glucosyl*-6-*phthalamic acid*, m.p. 183° (decomp.), also obtained from (I) and boiling dil. NaOH. (I) is hydrolysed by 50% AcOH at 100° to d-*glucosyl*-6-*phthalimide*, m.p. 192°, $[\alpha]_D^{19}$ +105·13° in C_5H_5N, which strongly reduces Fehling's solution and gives approx. correct results when titrated with I. When warmed with $NHPh{\cdot}NH_2$ (3 mol.) and AcOH (3 mol.) at 100° it gives a (?) *phenylhydrazone*, m.p. 171°, $[\alpha]_D^{20}$ +81·66° in C_5H_5N, whereas addition of it to a solution of $NHPh{\cdot}NH_2$ (3 mol.) in excess of 25% AcOH at 100° affords a "*semiosazone*," $C_{46}H_{42}O_{10}N_8$, m.p. 177°, $[\alpha]_D^{20}$ +80° in C_5H_5N. H. W.

Mechanism of carbohydrate oxidation. XIX. Preparation of disaccharide antipodes. L. C. Kreider and W. L. Evans (J. Amer. Chem. Soc., 1936, **58**, 797—800).—The appropriate acetobromopentose (1 mol.) added in 10 portions to a stirred mixture of $OH{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}OAc$ (2 mols.), Ag_2CO_3 (1 mol.), and "Drierite" (4 mols.) in C_6H_6 (25 mols.) gives β-d- (I), m.p. 102° (all m.p. are corr.), $[\alpha]_D^{21}$ +9·04° in $CHCl_3$, and β-l- (II), m.p. 102°, $[\alpha]_D^{21}$ −9·07° in $CHCl_3$, *-arabinosido-* and β-d-, m.p. 117°, $[\alpha]_D^{22}$ −60·3° in $CHCl_3$, and β-l-, m.p. 117°, $[\alpha]_D^{23}$ +60·2° in $CHCl_3$, *-xylosido-dihydroxyacetone tetra-acetates* in yields of 20—35%. The β-*dl*-arabinosido-derivative, from (I) and (II), has m.p. 116°. *Acetobromo*-l-*xylose*, m.p. 102°, $[\alpha]_D^{20}$ +212·2°, is prepared in 28% yield by Levene and Raymond's method (A., 1931, 336). The contribution of the group $OAc{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}CH<$ towards the mol. rotation is calc. to be about ±33,600 according to the position of the O ring. H. B.

Carbohydrates. XX. New syntheses of gentiobiose and 1-β-glucosidofructose. P. Brigl and O. Widmaier (Ber., 1936, **69**, [*B*], 1219—1227).—The constitution of the 5 : 6-benzylidene-1 : 2-*iso*propylideneglucose (I) of Levene *et al.* (A., 1923, i, 92; 1933, 378) is confirmed by converting it into the *acetate*, m.p. 104—105°, which passes when kept in 80% AcOH or catalytically hydrogenated into 1 : 2-*iso*propylideneglucose 3-acetate. The dibenzylidenefructose of Brigl *et al.* (A., 1932, 1115) is 2 : 3 : 4 : 5-dibenzylidenefructopyranose (II) since it readily affords a 1-p-*toluenesulphonate*, m.p. 171° (decomp.), $[\alpha]_D^{20}$ −34·9° in $CHCl_3$, and is converted by MeI and Ag_2O into 2 : 3 : 4 : 5-*dibenzylidene*-1-*methylfructose*, m.p. 113—114°, $[\alpha]_D^{20}$ −30·5° in $CHCl_3$, hydrolysed to non-cryst. 1-methylfructose, which affords 1-methyl-2 : 3 : 4 : 5-di*iso*propylidenefructose, m.p. 48—49°. The possibility that the $\dot{\vdots}CHPh$ and $\dot{\vdots}CMe_2$ residues are not similarly placed is excluded since the condensation of fructose with PhCHO in presence of $ZnCl_2$ gives also 2 : 3-*benzylidenefructose*, m.p. 181°, $[\alpha]_D^{20}$ −183·3° in C_5H_5N (*triacetate*, m.p. 112°, $[\alpha]_D^{20}$ −158·9° in $CHCl_3$; *tribenzoate*, $[\alpha]_D^{20}$ −327·1° in $CHCl_3$), which does not reduce Fehling's solution, is oxidised by $Pb(OAc)_4$, and is converted by PhCHO and $ZnCl_2$ into (II). Condensation of (I) with acetobromoglucose (III) and Ag_2O in $CHCl_3$ (free from EtOH) followed by regulated catalytic hydrogenation of the product leads to 3 : 5-*benzylidene*-1 : 2-iso*propylidene*-6-β-*glucosidoglucose tetra-acetate*, m.p. 166°, $[\alpha]_D^{20}$ −20·7° in $CHCl_3$, hydrolysed (Zemplén) to 3 : 5-*benzylidene*-1 : 2-iso*propylidene*-6-β-*glucosidoglucose*, m.p. 219°, $[\alpha]_D^{21}$ −13·9° in C_5H_5N, whence gentiobiose. Similarly (II) and (III) afford 2 : 3 : 4 : 5-*dibenzylidene*-1-β-*glucosidofructose tetra-acetate*, m.p. 144°, $[\alpha]_D^{20}$ −41·5° in $CHCl_3$, converted by NH_3–MeOH into 2 : 3 : 4 : 5-*dibenzylidene*-1-β-*glucosidofructose*, m.p. 176° after softening at 166°, $[\alpha]_D^{21}$ −40·5° in $CHCl_3$, which is catalytically hydrogenated to 1-β-*glucosidofructose*, m.p. 134—138°, $[\alpha]_D^{20}$ −59·4° in H_2O (*octa-acetate*, m.p. 128—129°, $[\alpha]_D^{20}$ −13·91° in $CHCl_3$). H. W.

Catalytic hydrogenation of sucrose. I. Hydrogenation with reduced nickel as catalyst. T. Tanno (Bull. Chem. Soc. Japan, 1936, **11**, 204—207).—Hydrogenation of sucrose at 100 atm. in presence of reduced Ni (prep. described) consists of a rapid reaction at 155—175° and a slow one at about 225°. In one experiment $3H_2$ were absorbed at 170—175°, giving *d*-mannitol (I) (0·5 mol.) and *d*-sorbitol (II) (0·5 mol.) with a mixture (III) of $OH{\cdot}CHMe{\cdot}CH_2{\cdot}OH$ and glycerol. In a second experiment $2H_2$ were absorbed at 155—160° giving (I) and (II) and a resinous mixture, which was further reduced at 170—175° to (III). Fructose gives similarly (I) and (II), but no (III), whence it is inferred that (III) is derived from the glucose portion of the mol. R. S. C.

Glycoside fissions in non-aqueous media. I. Alcoholysis of phenylglucosides. W. Voss and W. Wachs. **II. Alcoholysis of disaccharides.** W. Voss, H. Heisig, and W. Wachs (Annalen, 1936, **522**, 240—261, 261—268).—I. The reaction between various phenylglucosides and MeOH–HCl (0·5*N*) in presence of about 10% of MeCl at 25±0·05° is followed by titration of the PhOH formed with $p\text{-}NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ (Chapin, A., 1920, ii, 563). The mean vals. of $k \times 10^5$ are: α- and β-phenylglucosides, 82·8 and 49, respectively [corresponding vals. for hydrolysis with aq. 0·5*N*-HCl are 1·48 and 0·43, respectively]; α- and β-phenylglucoside tetra-acetates, 122 and 44·9, respectively [vals. for acetolysis with AcOH–HCl (0·5*N*) are 112 and 7·5, respectively]; *tetramethyl-α-*, b.p. 132·5—133°/0·05 mm., 145—146°/0·19 mm., $[\alpha]_D^{22}$ +158·5° in MeOH, and -β-, m.p. 78—78·5°, $[\alpha]_D^{22}$ −65·8° in MeOH, *-phenylglucosides* (prepared from the acetates and Me_2SO_4 in MeOH+50% NaOH at 55°), 29·8 and 7·6, respectively. Polarimetric data for the methanolyses show that Walden inversion occurs, *i.e.*, α- and β-methylglucosides are formed from β- and α-phenylglucosides, respectively; subsequent equilibration may take place. Much α- and a little β-methyl-*d*-glucoside are isolable from the reaction product from the above β-tetra-acetate. The first stage in the methanolysis is considered to be the addition of 1 mol. of HCl to give an oxonium-like compound.

II. Methanolysis (as above) of heptamethyl-β-methylcellobioside (I) and -methylmaltoside is followed polarimetrically. The data for (I) show that inversion occurs, *i.e.*, tetramethyl-α- and 2 : 3 : 6-trimethyl-β-methylglucosides are formed. The conclusions of Hess *et al.* (A., 1928, 1359) are thus invalidated. H. B.

Synthetic nucleosides. IV. Theophylline-5-methyl-*l*-rhamnofuranoside. P. A. Levene and J. Compton (J. Biol. Chem., 1936, **114**, 9—26; cf. A., 1931, 940).—*Theophylline-5-methyl*-l-*rhamnofuranoside* (I) is prepared and certain aspects of rhamnose derivatives are discussed. *Methyl*-β-5-*methyl*-l-*rhamnofuranoside*, b.p. 58—60°/0·3 mm., $[\alpha]_D^{25}$ +6·3° in H_2O, is obtained from *iso*propylidene-*l*-rhamnose (II), m.p. 92—93°, by

MeI–Na_2SO_4–Ag_2O, which proves the β-structure of (II). The α-glucoside (impure), b.p. 58—60°/0·3 mm., $[\alpha]_D^{24}$ −21·6° in H_2O, is obtained similarly from the *iso*propylidene compound (III), m.p. 79—81°, which proves the α-structure of (III). Both glucosides are hydrolysed by 1·5% H_2SO_4 to syrupy 5-*methyl*-1-*rhamnofuranose* (IV), the *phenylhydrazone*, m.p. 162—163°, $[\alpha]_D^{24}$ −18·4° → +8·1° in 7 days in C_5H_5N, of which with PhCHO affords the furanose with m.p. 102—103°, $[\alpha]_D^{25}$ −4·3° (const.) in H_2O, and with NHPh·NH_2 gives the *phenylosazone*, m.p. 123—124°, $[\alpha]_D^{24}$ +65·3° → +44·4° in 3 days in C_5H_5N–abs. EtOH (3 : 2). (IV) with cold Ac_2O–C_5H_5N gives the α-Ac_3 derivative (V), m.p. 115—116°, $[\alpha]_D^{24}$ −76·3° in dry MeOH, and the β-Ac_3 compound, b.p. 128—132°/0·8 mm., $[\alpha]_D^{24}$ −13·6° in dry MeOH. (IV) with MeOH–HCl gives amongst other substances *methyl*-α-5-*methyl*-1-*rhamnofuranoside* (VI), m.p. 59—60°, $[\alpha]_D^{23}$ −89·2° in H_2O. (V) and liquid HBr at room temp. (25 min.) give the furanosidyl bromide, which with Ag theophylline in PhMe gives (I), m.p. 212—213°, $[\alpha]_D^{26}$ −46·3° in H_2O. The crude mixture of 4- and 5-methyl-*l*-rhamnose triacetates with HBr–AcOH at 0° gives readily acetyl-4-methyl-*l*-rhamnosidyl bromide (VII) (previously considered to be the 5-Me compound), m.p. 104—105°, $[\alpha]_D^{26}$ −184·2° in $CHCl_3$ [also obtained from the pure 4-Me compound (VIII)], which with Ag theophylline in xylene at 80—90° gives *theophylline*-β-4-*methyl*-1-*rhamnopyranoside* (IX), m.p. 179—180°, $[\alpha]_D^{25}$ −71·8° in H_2O, also obtained by condensation of (VII) and hydrolysis of the resulting amorphous Ac_2 compound. (VII) with Ag_2O–MeOH or its Ac_2 derivative with $Ba(OMe)_2$–MeOH gives *methyl*-β-4-*methyl*-1-*rhamnopyranoside*, b.p. 105—106°/0·3 mm., $[\alpha]_D^{24}$ −13·9° in H_2O. Deacetylation of (VIII) affords about equal amounts of β- (XI), m.p. 125—126° [*phenylosazone*, m.p. 162—163°, $[\alpha]_D^{24}$ +25·8° → +14·3° in 2 weeks in C_5H_5N–EtOH (3 : 2)], and α-4-methyl-*l*-rhamnose, a syrup; the latter crude ether gives *methyl*-α-4-*methyl*-1-*rhamnopyranoside* (X), b.p. 104—105°/0·3 mm., $[\alpha]_D^{23}$ −50·2° in H_2O. Theophylline-β-*l*-triacetylrhamnopyranoside and $Ba(OMe)_2$–MeOH at 0° gives *theophylline*-β-1-*rhamnopyranoside*, m.p. 190—191°, $[\alpha]_D^{25}$ −89·3° in H_2O. (I) and (IX) are hydrolysed by 0·03*N*-HCl at 100° at about equal rates, but this is due to some peculiarity of the purine substituent, since (VI) is hydrolysed much faster than is (X). Mutarotation of (IV) could not be observed, but is assumed to occur very rapidly, since the presence of free CHO is contra-indicated by the absorption spectra. Mutarotation of (XI) in H_2O is rapid, resembling that of β-*l*-rhamnose. R. S. C.

Colloid behaviour of starch, cellulose, and glycogen.—See this vol., 795.

Highly polymerised compounds. CXXXVIII. Tearing of the thread molecules of cellulose by grinding. H. Staudinger and E. Dreher (Ber., 1936, **69**, [*B*], 1091—1098).—Intensive grinding of cellulose (I) under H_2O in an agate ball mortar causes degradation of the thread mols.; after 12 hr. the material has a mean degree of polymerisation about 300. The degraded cellulose nitrates obtained from the partly depolymerised materials form a polymeric-analogous series; on further grinding they suffer marked degradation. The non-degraded eucolloidal celluloses are tenacious and long-fibred, dissolve with marked swelling, and give highly viscous solutions. The degraded mesocolloidal celluloses of degree of polymerisation 300 are friable and readily sol. without swelling to solutions of low viscosity. The degradation of eucolloidal polystyrene when ground under H_2O is more pronounced than that of (I); it is also degraded when its solutions are forced through very fine holes in a Pt foil, whereas cellulose nitrate in amyl acetate is not greatly changed. H. W.

Hexamethylenetetramine compounds. P. Bouchereau (J. Pharm. Chim., 1936, [viii], **23**, 549—556).—The *compounds* $M(CaCl_2)_2,2H_2O$, $M(MgCl_2)_2,2H_2O$, and $M(MgS_2O_3)_2,2H_2O$ [$M = (CH_2)_6N_4$)] are described. Their antiseptic action is ascribed to free CH_2O. E. W. W.

Reaction of carbonyl chloride with hexamethylenetetramine.—See this vol., 689.

Characterisation and determination of tri-(hydroxyethyl)amine. D. Florentin and (Mme.) I. Ruiz (Ann. Falsif., 1936, **29**, 197—204).—The isolation of $N(C_2H_4{\cdot}OH)_3$ from its preps. and characterisation by means of the platinichloride, aurichloride, and *silicotungstate*, and its gasometric determination by decomp. with hypobromite are described. E. H. S.

Amino-acids and related compounds. IX. Electrolytic oxidation of proline and γ-aminobutyric acid. Y. Takayama (Bull. Chem. Soc. Japan, 1936, **11**, 138—141; cf. A., 1935, 92).—Electrolytic oxidation of proline gives mainly succinimide with a little $({\cdot}CH_2{\cdot}CO_2H)_2$ and a solution, which with hot $Ba(OH)_2$ gives NH_3, pyrrolidine, and $NH_2{\cdot}[CH_2]_3{\cdot}CO_2H$ (I) and which thus probably contained pyrrolidone. Similar oxidation of (I) gives NH_3 and $({\cdot}CH_2{\cdot}CO_2H)_2$. (I) is considered to be the primary product indicating preferential attack at the *tert.*-C. R. S. C.

Delayed oxidation of cysteine and ascorbic acid.—See this vol., 685.

Condensation products of glucidic acid derivatives with amines. O. von Schickh (Ber., 1936, **69**, [*B*], 976—974).—αβ-*Oxido*-β-*methyl*-n-*butyramide* (I), m.p. 121°, is obtained by the action of conc. aq. NH_3 on the corresponding Et ester or, preferably, by the action of Na on $CH_2Cl{\cdot}CO{\cdot}NH_2$ in $COMe_2$ at 0—2°. αβ-*Oxido*-β-*phenyl*-α-*methylpropion-amide*, m.p. 134°, and -*methylamide*, m.p. 116°, are derived from the corresponding Et ester. αβ-*Oxido*-β-*phenyl*-n-*valeramide* has m.p. 119—121°, $CH_2Cl{\cdot}CO{\cdot}NEt_2$, $NaNH_2$, and $COMe_2$ at 0—5° affords αβ-*oxido*-β-*methyl*-n-*butyrdiethyamide*, b.p. 122—124°/12 mm. Et αβ-oxido-β-phenyl-α-methylpropionate and NH_2Me–H_2O at 100° give β-*methylamino*-α-*hydroxy*-β-*phenyl*-α-*methylpropionmethylamide hydrochloride*, m.p. 240—242° (decomp.), hydrolysed by HCl (*d* 1·19) at 150° to β-*methylamino*-α-*hydroxy*-β-*phenyl*-α-*methylpropionic acid hydrochloride*, m.p. 224—225° (decomp.). NH_2Ph and (I) at 120° afford α-*anilino*-β-*hydroxy*-β-*methylbutyramide*, m.p. 102°, whilst *Et* α-*anilino*-β-

hydroxy-β-methylbutyrate, b.p. 171—175°/11 mm., m.p. 70—71°, is derived from the requisite Et ester and NH_2Ph at 170°. *Et α-methylanilino-β-hydroxy-β-methylbutyrate* has b.p. 172—174°/8 mm. When heated with the requisite amine (I) affords α-p-*phenetidino-*, m.p. 105°, α-p-*allyloxyanilino-*, ($+1H_2O$), m.p. 70—72°, α-*4-aminoantipyryl-*, m.p. 151°, and α-*2-aminopyridyl-*, m.p. 182—183°, *-β-hydroxy-β-methylbutyramide*. *α-6-Methoxy-δ-quinolylamino-β-hydroxy-β-methylbutyrdiethylamide* has m.p. 170—171° (decomp.). $NHPh\cdot NH_2$ and (I) at 150—180° give *4-hydroxy-1-phenyl-3 : 3-dimethylpyrazolid-5-one*, m.p. 182—183°, transformed by Me_2SO_4 and alkali into *4-hydroxy-1-phenyl-2 : 3 : 3-trimethylpyrazolid-5-one*, m.p. 109°. With $CO(NH_2)_2$ at 150—200° (I) yields *5-hydroxy-2 : 6-diketo-4 : 4-dimethylhydropyrimidine*, m.p. 196—197°. H. W.

Condensation of chloral with acid amides. Properties of $CH(OH)\cdot CCl_3$ group. A. N. Meldrum and M. G. Bhojraj (J. Indian Chem. Soc., 1936, **13**, 185—186; cf. Yelburgi *et al.*, A., 1934, 770).—Condensation of $CCl_3\cdot CHO$ with the appropriate $R\cdot CO\cdot NH_2$ affords *chloral-propion-*, m.p. 166—167°, -iso*butyr-*, m.p. 156—157°, -n-*valer-*, m.p. 142°, -n-*hexo-*, m.p. 139°, -n-*hepto-*, m.p. 125—126°, and *-phenylacet-*, m.p. 141°, *-amide*. Reduction of these with Zn–AcOH at <40° affords ββ-*dichlorovinyl-acet-*, m.p. 88—89°, *-propion-*, m.p. 100—101°, -iso*butyr-*, m.p. 84—85°, -n-*valer-*, m.p. 65—66°, -n-*hexo-*, m.p. 62—64°, -n-*hepto-*, m.p. 38—39°, and *-phenylacet-*, m.p. 90—92°, *-amide*. J. W. B.

Determination of carbamide by the Folin distillation method. Determination by steam-distillation. F. H. L. Taylor and M. A. Adams (J. Lab. Clin. Med., 1935, **20**, 983—985).—Steam-distillation is preferred to the original direct distillation. Ch. Abs. (*p*)

Preparation of carbamides. J. S. Buck and C. W. Ferry (J. Amer. Chem. Soc., 1936, **58**, 854).—*N*-Phenyl-*N*-*n*-butyl-, *N*-*o*-tolyl-*N*-*n*-propyl- and -*n*-butyl-, *N*-*m*-tolyl-*N*-ethyl- and -*n*-propyl-, and *N*-*p*-tolyl-*N*-*n*-propyl-carbamides are best prepared (61—91% yields) (cf. A., 1935, 1488) by cautious warming of NHArAlk (1 mol.) with $NO_2\cdot NH\cdot CO\cdot NH_2$ (1·15 mols.) in 95% EtOH (4—5 vols.). H. B.

Dialkylaminoacetylcarbamides. T. C. Daniels (J. Amer. Pharm. Assoc., 1936, **25**, 285—286).—The following aminoacetylcarbamides were prepared: *diethyl-*, m.p. 102°, *di*-n-*propyl-*, m.p. 123°, *di*-n-*butyl-*, m.p. 122°, *diiso*b*utyl-*, m.p. 68°, *di*-n-*amyl-*, m.p. 97°, and *diiso*a*myl-*, m.p. 99°. None possesses hypnotic properties. F. O. H.

Aliphatic carbimides and their conversion into α-aryl-β-alkylcarbamides. J. W. Boehmer (Rec. trav. chim., 1936, **55**, 379—391).—Alkylcarbimides are rapidly prepared (50—95% yields) by slow addition of $R\cdot COCl$ to activated NaN_3 (Nelles, A., 1932, 1118) in C_6H_6 or PhMe and then boiling until the theoretical vol. of N_2 has been evolved. Thus are obtained methyl-, ethyl-, *n*- and *iso*-propyl- and -butyl-carbimide. By addition of the appropriate NH_2Ar *s*-arylalkylcarbamides are obtained of which the following are new: s-p-*methoxy-*, m.p. 178°, p-*acetyl-*, m.p. 184°, m-, m.p. 119° and p-*chloro-*, m.p. 200°, and m-*bromo-phenyl-*, m.p. 134°, o-*phenylyl-*, m.p. 170°, β-*naphthyl-*, m.p. 187°, and 5-, m.p. 221°, and 8-*quinolyl-*, m.p. 192°, *-methylcarbamide*; s-p-*tolyl-*, m.p. 123°, p-*methoxy-*, m.p. 136°, p-*ethoxy-*, m.p. 147°, p-*acetyl-*, m.p. 123°, m-, m.p. 107°, and p-*chloro-*, m.p. 189°, m-, m.p. 110° and p-*bromo-phenyl-*, m.p. 197°, o-*phenylyl-*, m.p. 126°, α-, m.p. 177° and β-*naphthyl-*, m.p. 177°, 2-*pyridyl-*, m.p. 103°, and 5-, m.p. 186° and 8-*quinolyl-*, m.p. 167°, -n-*propylcarbamide*; s-p-*tolyl-*, m.p. 157°, p-*methoxy-*, m.p. 154°, p-*ethoxy-*, m.p. 183°, p-*acetyl-*, m.p. 153°, m-, m.p. 135°, and p-*chloro-*, m.p. 217°, m-, m.p. 133° and p-*bromo-phenyl-*, m.p. 212°, o-, m.p. 157°, and p-*phenylyl-*, m.p. 214°, α-, m.p. 200° and β-*naphthyl-*, m.p. 192°, 2-*pyridyl-*, m.p. 104°, 5-, m.p. 232°, and 8-*quinolyl-*, m.p. 184°, -iso*propylcarbamide*, s-*phenyl-*, m.p. 130°, p-*tolyl-*, m.p. 119°, p-*methoxy-*, m.p. 116°, p-*ethoxy-*, m.p. 146°, p-*acetyl-*, m.p. 125°, m-, m.p. 83°, and p-*chloro-*, m.p. 173°, m-, m.p. 75°, and p-*bromo-phenyl-*, m.p. 185°, o-*phenylyl-*, m.p. 120°, α-, m.p. 149°, and β-*naphthyl-*, m.p. 175°, 2-*pyridyl-*, m.p. 88°, 5-, m.p. 179°, and 8-*quinolyl-*, m.p. 134°, -n *butylcarbamide*; s-p-*tolyl-*, m.p. 154°, -p-*methoxy-*, m.p. 114°, -p-*ethoxy-*, m.p. 137°, -p-*acetyl-*, m.p. 72°, -m-, m.p. 114°, and -p-*chloro-*, m.p. 168°, -m-, m.p. 106°, and -p-*bromo-phenyl-*, m.p. 167°, -o-, m.p. 128°, and -p-*phenylyl-*, m.p. 191°, α-, m.p. 178°, and β-*naphthyl-*, m.p. 152°, -5-, m.p. 167°, and -8-*quinolyl-*, m.p. 164°, -iso*butylcarbamide*. With NHPhMe are obtained α-*phenyl*-α-*methyl*-β-n-, m.p. 46°, and -β-iso*butylcarbamide, m.p.* 54°. With H_2O RNCO gives $CO(NHR)_2$ and thus are obtained s-*di*-n-, m.p. 100°, and -*di*-iso-*propyl-*, m.p. 192°, -*di*-n-, m.p. 71°, and -*di*-iso-*butyl-*, m.p. 134°, *-carbamide*. J. W. B.

Complex compounds of semicarbazides.—See this vol., 692.

Synthesis of βγ-dihydropropylguanidine. S. Kawai and N. Sugiyama (Bull. Chem. Soc. Japan, 1936, **11**, 141—143).—Heating $NH_2\cdot CH_2\cdot CH(OBz)\cdot CH_2\cdot OBz$ with $CN\cdot NH_2$ or *O*-methyl-ψ-carbamide in dry EtOH or C_5H_5N at 120—130° causes only migration of Bz to yield $NHBz\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OBz$, but $NH_2\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$ and *S*-methyl-ψ-thiocarbamide hydriodide in EtOH at 100° give βγ-*dihydroxypropylguanidine*, an oil (*picrate*, m.p. 126°). R. S. C.

Reduction of nitroguanidine. V. Synthesis of γ-amino-α-methyl-, -α-ethyl-, and -α-*n*-butylguanidine. G. W. Kirsten and G. B. L. Smith (J. Amer. Chem. Soc., 1936, **58**, 800—801).—*γ-Amino-α-methylguanidinium iodide*, m.p. 121—122° [corresponding *sulphate*, m.p. 229—230° (decomp.), and *picrate*, m.p. 162—163°], is prepared from $SMe\cdot C(NH)\cdot NHMe,HI$ and N_2H_4 or from $SMe\cdot C(NH)\cdot NH\cdot NH_2,HI$ and NH_2Me. *γ-Amino-α-ethylguanidinium iodide*, m.p. 84·5—86° (corresponding *sulphate*, m.p. 161—163°, and *picrate*, m.p. 113—114·5°), and *γ-amino-α-*n-*butylguanidinium iodide*, m.p. 51—52°, are similarly obtained from $SMe\cdot C(NH)\cdot NHEt,HI$ and S-*methyl*-n-*butyl*iso*thiocarbamide hydriodide*, m.p. 88—89° (from $NH_2\cdot CS\cdot NHBu^a$

and EtOH–MeI), respectively. γ-Amino-α-phenylguanidine could not be similarly prepared. H. B.

Dyes from furfuraldehyde. T. Boehm and (Frl.) M. Grohnwald (Arch. Pharm., 1936, **274**, 318—326).—Hydrofurfuramide, CHR⁚N·CHR·N⁚CHR (R=2-furyl), and $CH_2(CN)_2$ (I) in EtOH give NH_3 and *γ-hydroxy-*$\Delta^{\alpha\gamma\epsilon}$*-heptatrienyl ααηη-tetracyanide* (II), violet, decomp. 225°, anhyd. (from MeOH), +0·66EtOH (0·33 mol. retained at 120°/0·1 mm.), +0·5Pr^{β}OH, +C_5H_5N, and +AcOH. The liberated NH_3 plays a part in the reaction, for (II) is also obtained from furfurylidenemalodinitrile (III) and NH_2R–EtOH, R being H, Me, Et, Ph, or, best, CH_2Ph, or $NHMe_2$– or $NHEt_2$–EtOH. The presence of a free OH in (II) is shown by formation (Ac_2O–C_5H_5N) of an *Ac* derivative (IV), decomp. 210°, +C_5H_5N and anhyd. (III) and $NH_2·CH_2Ph$ give also as by-product N-δ-*hydroxy-ζζ-dicyanohexatrienylbenzylamine* (V), blue, m.p. 161°, decomposes when recrystallised (*hydrochloride*, +MeOH, m.p. 140° after decomp. from about 140°), which with $NHPh·NH_2$ in a little EtOH gives N-δ-*hydroxy-ζζ-dicyano-*$\Delta^{\alpha\gamma\epsilon}$*-hexatrienyl-*N′*-phenylhydrazine*, m.p. 186° after sintering at 176°, and with (I) yields (III) immediately. (II) is thus formed by primary reaction to (V) or its analogous amine and further reaction thereof with (I). Furfurylidenecyanoacetamide and $NH_2·CH_2Ph$ in hot EtOH give similarly *γ-hydroxy-αη-dicyano-*$\Delta^{\alpha\gamma\epsilon}$*-heptatrienedicarbonamide*, +H_2O, m.p. 240—244° (decomp.). (II) and cold conc. HCl give a *substance*, possibly the *monoamide*, $C_{11}H_8O_2N_4$, m.p. 250—255° (decomp.), +1·5AcOH and +EtOH [*Ac* derivative (by Ac_2O–C_5H_5N), decomp. 215—220°]. Hydrogenation of (II) gives mixtures; if that (2% Pd–$BaSO_4$) of (IV) in $COMe_2$ is stopped after adsorption of $2H_2$, there is obtained a *substance*, possibly an amide, $C_{13}H_{12}O_2N_4$, m.p. 94—96°, which is sol. in KOH, from which after some hours HCl ppts. an *acid*, $C_{13}H_{15}O_5N_3$, m.p. 86°. R. S. C.

Arsinocarboxylic acids. H. J. Backer and C. H. K. Mulder (Rec. trav. chim., 1936, **55**, 357—370).—Arsinocarboxylic acids are prepared by the reaction $K_3AsO_3 + CHRBr·CO_2K \rightarrow AsO_3K_2·CHR·CO_2K + KBr$, and are isolated from their Pb salts. Kinetic studies in the case R=Me show that the rate increases with increasing concn. of reactants more rapidly than is required by a bimol. reaction and optimum yields (in parenthesis) are obtained when the mol. ratio $KOH/As_2O_3 = 6:1$. Thus are prepared arsinoacetic, α-*arsino-propionic* (I), m.p. 134° (71%) (*Ag*, Ba_3+5H_2O, and *Pb* salts), -n-*butyric*, m.p. 127° (68%) (*Ag*, *Ba*+H_2O, Ba_3+7H_2O, and *Pb* salts), -*valeric*, m.p. 116—117° (40%) (*Ba*+H_2O and +2H_2O, Ba_3, and *Pb* salts), -n-*hexoic*, m.p. 96° (33%), -n-*heptoic*, m.p. 82—83° (19%) (together with α-*hydroxy*-n-*heptoic acid*, m.p. 63°), -n-*octoic*-, m.p. 114° (12%) (with α-*hydroxy*-n-*octoic acid*, m.p. 79°), and n-*nonoic acid*, m.p. 115°. Similarly $CH_2Cl·CH_2·CO_2K$ gives β-*arsinopropionic acid* (II), m.p. 145° (56%) (Na_2+5H_2O, *Ag*, and *quinine* +6H_2O salts). Reduction (H_3PO_2) of (I) and (II) affords respectively α-, (⁚As·CHMe·$CO_2H)_2$, decomp. 85—90°, and β-*arsenopropionic acid*, m.p. 155—157°. K_3AsO_3 with either $CH_2Br·CHBr·CO_2K$ or CH_2⁚CBr·CO_2K gives α-*arsinoacrylic acid*, m.p. 159° (43%—50%) (*quinine* +6H_2O salt), reduced to α-*arsenoacrylic acid*, m.p. 180° (decomp.). *Phenylarsinoacetic acid*, sinters 100°, m.p. 110°, is similarly prepared. These acids titrate as dibasic acids to phenolphthalein. Some crystallographic data are given. J. W. B.

Organic reactions with silicon compounds. I. Use of silicon tetrafluoride in formation of esters and absorption reactions. J. A. Gierut, F. J. Sowa, and J. A. Nieuwland (J. Amer. Chem. Soc., 1936, **58**, 786—787).—Quant. yields of MeOAc and EtOAc and 20—60% yields of Pr^{β}OAc, Bu^{α}OAc, and Bu^{β}OAc are obtained from SiF_4 (from Na_2SiF_6, SiO_2, and conc. H_2SO_4), AcOH, and the appropriate alcohol (which forms an unstable 4 : 1 additive compound with SiF_4); NH_2Ac (for AcOH) similarly gives 13—20% of ester. With BzOH, the yield of ester is much smaller. Bu^{γ}OH and AcOH similarly afford 4·3% of Bu^{γ}OAc. Stable additive compounds are formed from SiF_4 and NH_3, NBu_3, and NH_2Ac. SiF_4 is not absorbed by PhOH, PhOPr^{β}, Et_2O, EtOAc, or AcOH. H. B.

Etherates of iodobismuthous and iodoantimonious acids.—See this vol., 690.

Electrolysis of magnesium methyl halides in ether solutions. W. V. Evans and E. Field (J. Amer. Chem. Soc., 1936, **58**, 720—724; cf. A., 1934, 517).—Electrolysis (apparatus described) of Et_2O–MgMeHal gives (mainly) CH_4 and C_2H_6, together with small amounts of C_2H_4 and CO_2 and (after hydrolysis) EtOH, Pr^{β}OH, and a non-volatile halogen-free saturated substance; H_2 and *iso*butene are not produced (cf. *loc. cit.*). The ratio $CH_4 : C_2H_6$ decreases rapidly with increase in c.d. to a limiting val. which is unaffected by concn. The efficiency of the electrolysis is, however, inversely ∝ the concn. above a limiting val. and decreases in the order Cl, Br, I. The following reactions occur: Me+H (from Et_2O, which also gives rise to the above minor products) → CH_4; $2Me \rightarrow C_2H_6$. The mechanism of formation of Me is: $Me_2Mg,MgX_2 \rightarrow [MeMgX_2]^- + [MgMe]^+$; $[MeMgX_2]^- - e \rightarrow Me + MgX_2$; $[MgMe]^- + e \rightarrow 1/2Mg + 1/2MgMe_2$. H. B.

Catalysed reaction of magnesium ethyl bromide with ethyl bromide. C. B. Linn and C. R. Noller (J. Amer. Chem. Soc., 1936, **58**, 816—819).—In agreement with Jolibois (A., 1927, 233) and contrary to Job and Dubien (*ibid.*, 233), the reaction between EtBr and MgEtBr in presence of Cu_2Cl_2 is heterogeneous; no conclusions concerning the mechanism can, therefore, be reached from rate measurements. The catalyst is Cu (formed by reduction of the Cu_2Cl_2 with MgEtBr). Ordinary Cu does not catalyse the reaction; Cu prepared by reduction (H_2) of powdered CuO is fairly active. Solutions of $MgEt_2$ behave in exactly the same manner as MgEtBr. The following reactions are considered to occur: $2Cu + C_2H_4 + C_2H_6 + MgBr_2 + MgCl_2 \leftarrow Cu_2Cl_2 + 2MgEtBr \rightarrow 2Cu + 2C_2H_4 + H_2 + MgBr_2 + MgCl_2$. H. B.

Catalysts for autoxidation of saturated cyclic hydrocarbons.—See this vol., 685.

***cyclo*Propane. Raman spectrum and polymerisation by ultra-violet light.**—See this vol., 777.

Ultra-violet absorption of *cyclo*propane and propylene; their preparation and b.p. A. A. Ashdown, L. Harris, and R. T. Armstrong (J. Amer. Chem. Soc., 1936, **58**, 850—852).—*cyclo*Propane (I), b.p. −32·89±0·05°/755·9 mm. [prep. (cf. Gustavson (A., 1888, 240) from $(CH_2)_3Br_2$ (3 mols.) and Zn wool (4 mols.) in EtOH with exclusion of H_2O, thus practically eliminating reduction to C_3H_8], and C_3H_6, b.p. −47·67±0·1°/759·1 mm. (from $Pr^{\beta}OH$ and H_3PO_4, whereby a considerable amount of $Pr_2{}^{\beta}O$ is produced), show continuous absorption in the ultra-violet; mol. extinction coeffs. are determined. (I) resembles a paraffin hydrocarbon. H. B.

Synthesis of monosubstituted *cyclo*pentane homologues with branched side chains. B. A. Kasanski, A. F. Plate, and K. M. Gnatenko (Ber., 1936, **69**, [*B*], 954—960).—The action of Grignard's reagents on *cyclo*pentanone and subsequent dehydration of the *tert.* alcohols thus produced does not afford monosubstituted *cyclo*pentanes in satisfactory yield. Hydrogenation of dimethylfulvene, b.p. 45—47°/12 mm., from *cyclo*pentadiene and $COMe_2$, proceeds slowly in EtOH with Pd–Ni, more rapidly is AcOH (Pd-black) giving iso*propyl*cyclo*pentane*, b.p. 123—124°/731·6 mm. Similarly methylethyl- and diethyl-fulvene afford sec.-*butyl*cyclo*pentane*, b.p. 152·5—153·5°/763·7 mm., and sec.-*amyl*cyclo*pentane*, b.p. 174—176°, respectively. Hydrogenation of diphenylfulvene (I) (Ni–EtOH) at 100—120°/40 atm. gives a *substance* $C_{18}H_{18}$, m.p. 62·5—63°, which becomes liquid when exposed to air. In EtOH (Pt or Pd) (I) absorbs 2 H very readily and a further 2 H more slowly, after which reaction nearly ceases. The crude product is, however, converted by Na in EtOH into *diphenylmethyl*cyclo*pentane*, m.p. 32·5—33°. H. W.

Multiplanar isomerism of *cyclo*hexanes. R. F. Miller and R. Adams (J. Amer. Chem. Soc., 1936, **58**, 787—791).—Assuming that multiplanar forms of the *cyclo*hexane ring are possible, the theoretical no. of isomerides of the types aaC_6H_8bb, aaC_6H_8bc, and abC_6H_8cd is 4 (3 "C," 1 "Z"), 8 (6 "C," 2 "Z"), and 16 (12 "C," 4 "Z"), respectively. Fractional crystallisation of 4-methyl- and 4 : 4-dimethyl-*cyclo*hexane-1 : 1-diacetic acids and 4 : 4-dimethyl*cyclo*hexane-1-carboxylic-1-acetic acid, their NH_4 salts, and anhydrides has failed to reveal the existence of more than one form (cf. Qudrat-i-Khuda, A., 1931, 1055; 1935, 1236; Goldschmidt and Gräfinger, A., 1935, 489; Desai and Hunter, *ibid.*, 1495).

Reduction of 4-methyl-4-dichloromethyl-$\Delta^{2:5}$-*cyclo*hexadienone with H_2 and Raney Ni in EtOH–NaOH (calc. amount to neutralise HCl produced) gives 4 : 4-dimethyl*cyclo*hexanol, b.p. 68°/7 mm., m.p. 37°, oxidised (method: von Auwers and Keil, A., 1903, i, 100) to 4 : 4-dimethyl*cyclo*hexanone (I), m.p. 40—42°. ββ-Dimethylglutaric acid is reduced [H_2 (250 atm.), Cu–Cr oxide] to *γγ-dimethylpentane*-αε-*diol*, b.p. 132°/1 mm., converted by $SOCl_2$ into αε-dichloro-, b.p. 135°/80 mm., and thence by NaCN in 50% EtOH into αε-*dicyano-γγ-dimethylpentane*, b.p. 155—157°/7 mm., which is hydrolysed (EtOH–conc. H_2SO_4) to *Et γγ-dimethylpimelate*, b.p. 135°/7 mm. Hydrolysis of this with aq. $Ba(OH)_2$, evaporation of the reaction mixture to dryness, and subsequent heating to 300° (bath) gives (I). *Et* 4 : 4-*dimethyl*cyclo*hexylidenecyanoacetate*, b.p. 155°/7 mm., m.p. 50° [from (I), $CN{\cdot}CH_2{\cdot}CO_2Et$ (II), and piperidine], with aq. EtOH–KCN followed by hydrolysis (conc. HCl) of the resultant K salt, affords 4 : 4-*dimethyl*cyclo*hexane*-1-*carboxylic*-1-*acetic acid*, m.p. 189° (bloc Maquenne) (*anhydride*, m.p. 124°). (I), (II), and NH_3 in EtOH give 4 : 4-*dimethyl*cyclo*hexane*-1 : 1-*dicyanoacetic acid imide*, m.p. 230° (decomp.), hydrolysed (70% H_2SO_4) to 4 : 4-*dimethyl*cyclo*hexane*-1 : 1-*diacetic acid*, m.p. 213—218° (tube), 230° (bloc) (*anhydride*, m.p. 86°). H. B.

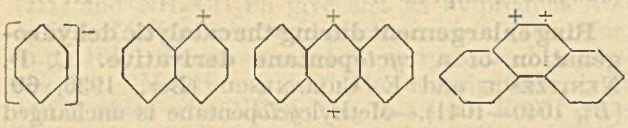
Ring enlargement during the catalytic dehydrogenation of a *cyclo*pentane derivative. C. D. Nenitzescu and E. Cioranescu (Ber., 1936, **69**, [*B*], 1040—1041).—Methyl*cyclo*pentane is unchanged when passed over Pt–C at 310° or 350°. Under similar conditions small amounts of $C_{10}H_8$ are obtained from 1-methylhydrindene or 1-*methylhexahydrohydrindene*, b.p. 182—183°. H. W.

Kinetics of formation and decomposition of di*cyclo*pentadiene.—See this vol., 684.

Fused carbon rings. X. Fundamental properties of 0 : 3 : 3-*dicyclo*octane ring. J. W. Barrett and R. P. Linstead (J.C.S., 1936, 611—616).—Reduction of pure samples of *cis*- (I) and *trans*-β-0 : 3 : 3-*dicyclo*octanone (Clemmensen or Kishner–Wolff methods) affords *cis*- (II) and *trans*- (III), m.p. −29° (corr.) (A., 1935, 750 gives m.p. −36°), -0 : 3 : 3-*dicyclo*octane, the heats of combustion of which are 1197·7 and 1203·8 kg.-cal. per mol. for liquid at const. vol. (Becker). (II) is not dehydrogenated by Pt–asbestos (active to decalin) at 300—320° (H_2 atm.). (I) and $CH_2Ph{\cdot}MgCl$ afford 2-*benzyl*-cis-0 : 3 : 3-dicyclo*octan*-2-*ol*, m.p. 66—67°, and a liquid *stereoisomeride*, both dehydrated by $H_2C_2O_4$ at 120° to 2-*benzylidene*-cis-0 : 3 : 3-dicyclo*octane*, b.p. 126—127°/3 mm.: this with Se at 300—330° is partly decomposed and partly unchanged. Under the same conditions *trans*-2-benzyloctalin (by dehydration of trans-2-*benzyl*-2-*decalol*, b.p. 170°/3 mm.) readily gives $2\text{-}C_{10}H_7{\cdot}CH_2Ph$. Reduction of (I) with Na–moist Et_2O or catalytically (Adams) gives cis-0 : 3 : 3-dicyclo*octan*-2-*ol*, b.p. 85—86°/10 mm. (*H phthalate*, m.p. 72°; *phenylurethane*, m.p. 116°), which is a mixture of stereoisomerides, unchanged by Se at 300—310°, conditions under which *trans*-β-decalol is also stable. With $AlCl_3$ at room temp. (II) is converted mainly into (the more strained) 1 : 2 : 3-*dicyclo*octane, identical with a synthetic specimen (Komppa *et al.*, this vol., 333). (III) is unchanged by passage with H_2 over Pt–asbestos (active to C_6H_6) at 200°. J. W. B.

Reactivity of aromatic hydrogen atoms. O. Zwecker (Ber., 1936, **69**, [*B*], 993—997; cf. A., 1935, 1112).—The general hypothesis is that an aromatic H under the influence of an *o*-substituent, *B*, reacts more rapidly or more slowly with a given reagent than when under the influence of a substituent *C* according as the compound H*B* reacts more rapidly or more slowly than H*C*. In this connexion the following changes are considered: chlorination, sulphonation, and nitration of NH_2Ph and its *N* derivatives; nitration of PhMe, CH_2PhCl, $CHPhCl_2$, $CPhCl_3$, PhCHO, and BzOH in comparison with the corresponding CH_4 compounds; chlorination of $PhNO_2$ and nitration of PhCl. H. W.

Influence of solvent on the course of chemical reactions. VIII. Evidence of the ionoid course of substitution. Formulation of aromatic hydrocarbons. K. Lauer and R. Oda (Ber., 1936, **69**, [*B*], 1061—1065).—Evidence in favour of the view that the aromatic hydrocarbons have the annexed, dynamic limiting constitutions (in which — and +



denote the anionoid and cationoid nature of a position) is found in the observation that the chlorination of C_6H_6 in AcOH is greatly hampered by HCl or chlorides whereas that of the condensed aromatic hydrocarbons is greatly accelerated. H. W.

Condensation of benzene with unsaturated hydrocarbons and their halogen derivatives in presence of acid catalysts. R. Truffault (Compt. rend., 1936, **202**, 1286—1289).—With P_2O_5 much polymerisation occurs in the condensation of unsaturated hydrocarbons with C_6H_6. C_2H_4 and C_3H_6 give, respectively, some PhEt and $PhPr^a$, but C_5H_{10} gives only $(C_5H_{10})_2$, and *cyclo*hexene (I) gives mainly its dimeride and some phenyl*cyclo*hexane (II). No such polymerisation occurs when H_2SO_4 at room temp. is used. Thus (I) gives a 70% yield of (II) and 25% of C_{18} hydrocarbons, mainly *p*-di*cyclo*hexylbenzene. C_6H_6 and $CH_2{:}CH{\cdot}CH_2Cl$ afford β-chloro*iso*propylbenzene (III), converted by KCN into the nitrile, hydrolysed to the amide of β-phenyl-β-methylpropionic acid, which is readily obtained by the action of CO_2 on the Mg compound of (III). J. W. B.

Addition and additive products of halogens and benzene derivatives. V. Addition of chlorine to three trichlorobenzenes. T. van der Linden (Rec. trav. chim., 1936, **55**, 315—324).—The rate of addition of liquid Cl_2, at room temp. in sunlight, to 1 : 2 : 3- (I), 1 : 2 : 4- (II), and 1 : 3 : 5- (III) -$C_6H_3Cl_3$ decreases in this order. (I) affords only one isomeride of 1 : 1 : 2 : 2 : 3 : 3 : 4 : 5 : 6-*nonachloro*-cyclo*hexane*, m.p. 80°. (II) gives a series of (unseparable) mixed crystals, m.p. 112—114°, 120°, 135°, and 82°, of two isomerides of 1 : 1 : 2 : 2 : 3 : 4 : 4 : 5 : 6-$C_6H_3Cl_9$ (stable to boiling EtOH), and 1 : 2 : 2 : 3 : 4 : 4 : 5 : 6-*octachloro*-Δ^6-cyclo*hexene*, m.p. 107—108°, obtained by loss of HCl from a third unstable isomeride. (III) affords one isomeride of 1 : 1 : 2 : 3 : 3 : 4 : 5 : 5 : 6-*nonachloro*cyclo*hexane*, m.p. 116°. Addition is assumed to occur most readily at double linkings unsubstituted in both Kekulé forms, and these and previous results, and the substitution of PhCl, are discussed on this basis. J. W. B.

Tin vanadate as catalyst in the oxidation of toluene.—See this vol., 686.

Halogenation. XIV. Iodination of aromatic hydrocarbons and bromotoluenes. P. S. Varma and C. Sreenivasmurthyachar. **XV. Chlorination and bromination of cumene and *p*-cymene.** P. S. Varma and M. K. Srinivasan. **XVI. Bromination and iodination of mesitylene.** P. S. Varma and T. S. Subrahmanian (J. Indian Chem. Soc., 1936, **13**, 187—188; 189—191; 192—193).—XIV. Iodination of several aromatic hydrocarbons is effected by heating with I–fuming HNO_3–conc. H_2SO_4 on a water-bath.

XV. Passage of Cl_2 into cumene containing 15% I–AcOH in diffused sunlight affords *p*-chlorocumene and p-*chloro*-α-*chloro*iso*propylbenzene*, m.p. 181°. By similar methods are obtained p-*bromo*-, m.p. 226°, and p-*chloro*-α-*bromo*iso*propylbenzene*, m.p. 207°. 2-Chloro-*p*-cymene with Br–Fe affords its 5-*Br*-derivative, b.p. 247°. The products obtained using various halogen-carriers are tabulated.

XVI. Mesitylene (I) with Br–fuming HNO_3 gives its 2-Br-derivative, and, with Br–AcOH–fuming HNO_3, its 2 : 4-Br_2- and 2 : 4 : 6-Br_3-derivatives. (I) and I–AcOH–NO_2SO_2H give the 2 : 4-I_2-derivative further iodinated to the 2 : 4 : 6-I_3-derivative. 2-Bromomesitylene similarly gives 2-*bromo*-4-*iodo*-*mesitylene*, m. p. 175—176°. J. W. B.

Toluene series. V. Sulphinic and sulphonic acids of the mono- and di-chlorotoluenes. W. A. Silvester and W. P. Wynne. **VI. Nitration of the 4-chlorotoluene-2- and -3-sulphonic acids, 3-chlorotoluene-6-sulphonic acid, and their sulphonyl chlorides.** W. P. Wynne. **VII. Nitration of 2-chlorotoluene-4- and -5-sulphonic acids and their sulphonyl chlorides.** (Miss) E. G. Turner and W. P. Wynne (J.C.S., 1936, 691—696, 696—707, 707—716; cf. J.C.S., 1898, **73**, 730).—V. The orientation of the sulphonation products of the isomerides, $C_6H_3MeCl_2$ (J.C.S., 1892, **61**, 1042; Proc. C.S., 1895, **11**, 151), is established by synthesis. In all cases orientation is normal, except that 2 : 3-$C_6H_3MeCl_2$ gives 89% of 6- and 11% of 5-sulphonic acid (cf. 10% of 6- and 90% of 4-NO_2-derivative) and that *p*-C_6H_4MeCl gives 86% of 2- and 14% of 3-sulphonic acid (cf. 42% of 2- and 58% of 3-NO_2-derivative). *m*-$C_6H_4Me{\cdot}NHAc$ with Cl_2 (1 mol.) in AcOH gives mixtures of Cl- with 4 : 6- and 2 : 6-Cl_2-derivatives, and with Cl_2–H_2O a poor yield of 6-chloro-*m*-toluidine; S_2Cl_2 (1 part) in CS_2 (5 parts) gives, however, 80% of 6-, 12% of 4-, and 8% of 2-Cl-derivative, and further reaction with S_2Cl_2 (0·8 part) in CS_2 gives a mixture containing much 4 : 6- and some 2 : 6-Cl_2-compound. The diazonium sulphite of 3-chloro-*p*-toluidine with Cu-bronze gives a good yield of 3-*chlorotoluene*-4-*sulphinic acid*, m.p. 110° (*Ba* salt, $+4H_2O$), oxidised by $KMnO_4$ to the *sulphonic acid* (*K* salt; *chloride*, m.p. 46°; *amide*, m.p. 186°). Similar reactions give 3-*chlorotoluene*-6-*sulphinic* (*Ba* salt, $+4H_2O$) and sulphonic *acid* [chloride, m. p. 54°; amide, m.p. 185°; obtained (*loc. cit.*) from *m*-C_6H_4MeCl], 2 : 3-*dichlorotoluene*-6-*sulphinic*, m.p. 133° (*Ba* salt, $+4H_2O$), and -sulphonic *acid* (chloride, m.p. 51—52°; amide, m.p. 228°),

-4-*sulphinic*, m.p. 142° (*Ba* salt, $+H_2O$), and -sulphonic *acid* (*K* salt; *chloride*, m.p. 40—41°; *amide*, m.p. 237°), 2 : 4-*dichlorotoluene*-5-*sulphinic*, m.p. 132° (*K* salt), and sulphonic acid [*K* salt, $+2H_2O$ (only one lost at 190°); chloride, m.p. 72°; amide, m.p. 176°; obtained from 2 : 4-$C_6H_3MeCl_2$], 2 : 6-*dichlorotoluene*-3-*sulphinic* (poor yield), m.p. about 105° (*Ba* salt, $+4H_2O$), and -sulphonic *acid* (chloride, m.p. 59°; amide, m.p. 203°; obtained from 2 : 6-$C_6H_3MeCl_2$), 3 : 5-*dichlorotoluene*-4-, m.p. about 127°, and -2-*sulphinic acid*, m.p. 115—116° (*Ba* salt, $+4H_2O$), and -4- (*K* salt, $+H_2O$; *chloride*, m.p. 56°; *amide*, m.p. 154—155°) and -2-sulphonic acid (*chloride*, m.p. 43°; amide, m.p. 168°; obtained from 3 : 5-$C_6H_3MeCl_2$). 5 : 6-Dichloroacet-*o*-toluidide, m.p. 143°, with 50% H_2SO_4 at 90° gives 5 : 6-dichloro-*o*-toludine, m.p. 33°, b.p. 288—290°/739 mm. (sulphate). 3-Chloro-*o*-toluidine-5-sulphonic acid (*Ba* salt, $+3H_2O$) with 75% H_2SO_4 at 160° gives 3-chloro-*o*-toluidine, an oil (Ac derivative, m.p. 163°), which affords (Sandmeyer) 1 : 2 : 3 : 5-$C_6H_2MeCl_2\cdot SO_3H$ (97% yield; chloride, m.p. 88°; amide, m.p. 184—185°; *Ba*, $+3H_2O$, and *Na*, $+0{\cdot}5H_2O$, salts). Nitration of 2 : 3-$C_6H_3MeCl_2$ is best effected by H_2SO_4–HNO_3 (*d* 1·42) at <50° and gives a mixture, reduced to a mixture of 2 : 3-dichloro-*p*-, m.p. 40°, b.p. 271—276°/40 mm. (Ac derivative, m.p. 131°), and -*o*-toluidine (10%), which is best separated by fractional neutralisation of the hydrochlorides; similar nitration of 2 : 6-$C_6H_3MeCl_2$, b.p. 199—200°, gives the 3-NO_2-compound, m.p. 50°, and on reduction solely 2 : 6-dichloro-*m*-toluidine, m.p. 57°, b.p. 266—268°. If Cl_2 (1 mol.) is passed into 5-chloroacet-*o*- or 3-chloroacet-*p*-toluidide in cold AcOH and the solution is warmed to 75° after some hr. and diluted with H_2O, there are formed the 3 : 5-, m.p. 180°, and 2 : 3-Cl_2-, m.p. 198°, -compounds, respectively, which are hydrolysed to the bases, m.p. 45° and b.p. 249°/772 mm., respectively.

[With J. KENNER.] The formation of 6- and 5-SO_3H derivatives from 2 : 3-$C_6H_3MeCl_2$ is confirmed (cf. J.C.S., 1902, **81**, 1334).

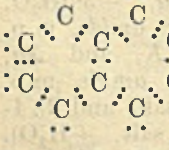
VI. The products of nitration of 1 : 4 : 2- (I), 1 : 4 : 3- (II), and 1 : 3 : 6- (III), -$C_6H_3MeCl\cdot SO_3H$ can be separated only by way of the acid chlorides (obtained from the Na salts by PCl_5–$POCl_3$). Orientations are determined by the reactions, $NO_2\cdot C_6H_2MeCl\cdot SO_3H \rightarrow NH_2\cdot C_6H_2MeCl\cdot SO_3H \rightarrow C_6H_2MeCl_2\cdot SO_3H \rightarrow C_6H_3MeCl_2 \rightarrow C_6H_3Cl_2\cdot CO_2H$. (II) is remarkable in giving 31% of 5-, 15% of 6-, and 54% of 2-NO_2-compound (although only 64% of the total material is accounted for), whereas the corresponding acid chloride gives 78% of 5-, 22% of 2-, and no 6-NO_2-compound. All nitrations are effected by fuming HNO_3–H_2SO_4 at or about room temp. (II) gives 4-*chloro*-5- [*Ba*, $+2H_2O$, *K*, $+H_2O$, and *Na*, $+H_2O$, salts; *chloride*, m.p. 62·5° (crystallographic data given); *amide*, m.p. 196°], -6- (*Ba*, $+2H_2O$, *K*, and *Na*, $+H_2O$, salts; *chloride*, m.p. 92°; *amide*, m.p. 188°), and -2-*nitrotoluene*-3-*sulphonic acid* (*Ba*, $+8H_2O$, *K*, and *Na*, $+3H_2O$, salts; *chloride*, m.p. 122°; *amide*, m.p. 177°; with conc. H_2SO_4 at 220° affords 4 : 2-$C_6H_3MeCl\cdot NO_2$), which gives ("reduced" Fe–dil. H_2SO_4) 4-*chloro*-5-, $+H_2O$ (*Ba*, $+1{\cdot}5H_2O$, *K*, $+H_2O$, and *Na*, $+H_2O$, salts), -6- (*Ba*, $+9H_2O$, *K*, $+H_2O$, and *Na*, $+5H_2O$, salts), and -2-*aminotoluene*-3-*sulphonic acid* (*Ba*, $+0{\cdot}5H_2O$, decomp. 140°, *K*, and *Na*, $+1{\cdot}5H_2O$, salts), and thence 4 : 5- (*Ba*, *K*, $+H_2O$, and *Na*, $+H_2O$, salts; *chloride*, m.p. 64°; *amide*, m.p. 158°), 4 : 6- (*Ba*, $+2H_2O$, *K*, and *Na*, $+1{\cdot}5H_2O$, salts; *chloride*, m.p. 72°; *amide*, m.p. 178°), and 2 : 4-*dichlorotoluene*-3-*sulphonic acid* (*Ba*, $+H_2O$, *K*, and *Na*, $+H_2O$, salts; *chloride*, m.p. 19·5°; *amide*, m.p. 188°), respectively, converted by H_3PO_4 and steam at about 240° into the dichlorotoluenes. (I) or its chloride gives mainly 4-*chloro*-6- [*Ba*, $+4H_2O$, *K*, $+0{\cdot}5H_2O$, and *Na*, $+1{\cdot}5H_2O$, salts; *chloride*, m.p. 60° (crystallographic data given); *amide*, m.p. 167°] with some -3-*nitrotoluene*-2-*sulphonic acid* (*Ba* salt, $+5H_2O$, *K*, and *Na*, $+4H_2O$, salts; *chloride*, m.p. 154°; *amide*, m.p. 183°), converted into 4-*chloro*-6-, $+H_2O$ (*Ba*, *K*, $+H_2O$, and *Na*, $+H_2O$, salts), and -3-*amino*- (*Ba*, *K*, $+H_2O$, and *Na*, $+H_2O$, salts), 4 : 6- (*Ba*, *K*, $+H_2O$, and *Na*, $+H_2O$, salts; *chloride*, m.p. 54°; *amide*, m.p. 186°) and 3 : 4-*dichloro-toluene*-2-*sulphonic acid* (*Ba*, *K*, and *Na*, $+H_2O$, salts; *chlcride*, m.p. 49°; *amide*, m.p. 186°). (III) or its chloride (IV) gives mainly 3-*chloro*-4- (*Ba*, $+3H_2O$, *K*, and *Na*, $+H_2O$, salts; *chloride*, m.p. 116°; *amide*, m.p. 170°) and a very little -2-*nitrotoluene*-6-*sulphonic acid* (*Ba*, *K*, and *Na* salts; *chloride*, m.p. 96°; *amide*, m.p. 176°), converted into 3-*chloro*-4- (*Ba*, $+2H_2O$, *K*, and *Na*, $+H_2O$, salts) and -2-*amino*-, $+H_2O$, 3 : 4- (optical data of chloride given) and 2 : 3-*dichloro-toluene*-6-*sulphonic acid* (*Na*, $+H_2O$. salt; *chloride*, m.p. 54°), respectively. (IV) is obtained with a little 4 : 4′-*dichloro*-3 : 3′-*dimethyldiphenylsulphone*, m.p. 130°, from *m*-C_6H_4MeCl and $ClSO_3H$ in CS_2.

VII. Nitration (as above) of 1 : 2 : 4-$C_6H_3MeCl\cdot SO_3H$ gives 95% of 5- and 5% of 6-NO_2-derivative, 80% and 20%, respectively, being obtained from the chloride. 1 : 2 : 5-$C_6H_3MeCl\cdot SO_3H$ and its chloride give 67 and 98% of the 3- and 33 and 2% of the 4-NO_2-derivative, respectively. K chloronitrotoluenesulphonates, in which the NO_2 has both an *o*-SO_3K and a *p*-Cl, give with PCl_5–$POCl_3$ poor yields of sulphonyl chloride with much dichloronitrotoluenesulphinyl chloride. Orientations are established as above. The following are described. 2-*Chloro*-5- (*K* salt; crystallographic data of chloride given) and -6-nitro- (*K* salt), -5- (*Ba*, $+H_2O$, and *K*, $+2H_2O$, salts) and -6-*amino*- (*K* salt), and 2 : 6-*dichlorotoluene*-4-*sulphonic acid* (*K* salt). 2-*Chloro*-5-*nitro*- (*Ba*, $+H_2O$, and *Na* salts) and -*amino*-, $+0{\cdot}33H_2O$ (*Na* salt), and 3 : 5-*dichloro-toluene*-6-*sulphonic acid* (*Ba*, *K*, and *Na*, $+H_2O$, salts; *chloride*, m.p. 38°; *amide*, m.p. 180°). 2-*Chloro*-3- (*Ba*, $+3{\cdot}5H_2O$, *K*, and *Na* salts; *chloride*, m.p. 52°; *amide*, m.p. 201°) and -4-*nitro*- (*Ba*, $+2H_2O$, *K*, and *Na*, $+1{\cdot}5H_2O$, salts; *chloride*, m.p. 97°; *amide*, m.p. 172°), -3- (*K* salt) and -4-*amino*- (*Na* salt) and 2 : 4-*dichloro-toluene*-5-*sulphonic acid* (*Na* salt, $+H_2O$). 2 : *x*-*Dichloro*-5-*nitrotoluene*-4-, decomp. 128° (darkening at 95—100°), and -6-*sulphinyl chloride*, m.p. 119° (decomp.); the former is oxidised by dil. HNO_3 to a *sulphonic acid* (*K* salt); both react with $AgNO_3$ in dil. HNO_3 (1Cl removed), 1% aq. NaOH, and $Fe(OH)_3$.

[Addendum. G. M. Bennett.] Summary of the above results shows the high *o*- and less high *p*-directing power of Me and SO_3H diminished as expected by conversion of SO_3H into SO_2Cl owing to the higher electron-attracting power of SO_2Cl, inability of SO_2Cl to ionise, and lesser attraction of SO_2Cl for HNO_3. Similarly $PhSO_2Cl$ gives 90% of *m*-NO_2-derivative, whereas $PhSO_3H$ gives 27% of *o*-compound. R. S. C.

Reaction between triarylmethyl halides and magnesium phenyl bromide. II. C. S. Schoepfle and S. G. Trepp (J. Amer. Chem. Soc., 1936, 58, 791—794; cf. A., 1932, 1240).—MgPhBr (in Et_2O) and CPh_3Cl or CPh_3Br (in C_6H_6) afford 5—7·5% of CPh_4 and 50—77% of diphenyldiphenylylmethane (I). With Et_2O-free MgPhBr and CPh_3Cl (in C_6H_6, PhMe, PhBr, $C_2H_4Cl_2$, or dioxan) 20—25% of CPh_4 is obtained; (I) could not be isolated. In the latter case there appears to be a smaller tendency to favour the quinonoid form (cf. *loc. cit.*) of the CPh_3Cl. The rate of reaction of the benzenoid form is very slow in comparison with the quinonoid. Other products isolated in the first-named (?) reaction are $CHPh_3$ (5%), phenyldi(diphenylyl)- (3%), tri(diphenylyl)- (trace), and *p*-phenyltetraphenyl- (0·6%) -methanes; reaction mechanisms are discussed briefly. 4 : 4′ : 4″-*Tribromo*-, m.p. 234—235° (43—45% yield), 4 : 4′ - 4″-*trichloro*-, m.p. 207—207·5° (38—49%), and 4 : 4′ : 4″-*trimethyl*-, m.p. 177—178° (31—41%), -*tetraphenylmethane* are prepared from MgPhBr (in Et_2O) and CAr_3Cl (in C_6H_6); the higher yields (cf. above) are ascribed to the lessened tendency of the CAr_3Cl to become quinonoid. H. B.

Influence of solvent on the course of chemical reactions. VII. Spectra of aromatic hydrocarbons in solution. K. Lauer (Ber., 1936, 69, [*B*], 986—993).—The absorption spectrum of $C_{10}H_8$ has been observed for the vapour and cryst. states and in *n*-hexane, Et_2O, EtOH, MeOH, *cyclo*hexene, and C_6H_6. The displacements show that the bands of longest λ are due in the first place to the polar, cationoid positions of the mol. which must be an α-position. Such polar atoms not only attract the polar positions of the solute indirectly but also cause production of associates, solvates, or mol. compounds. Further bands are due to the entire mol. and show the peculiarities observed with C_6H_6. The second part of the spectrum, in the region of shorter λ, is due to the aromatic nucleus and the displacements correspond qualitatively with those of C_6H_6. To $C_{10}H_8$ the constitution (I) is therefore assigned, this being regarded as a limiting formula. Similar limiting formulæ are proposed for anthracene indicating the strong cationoid polarity of the 9 : 10 positions. In general the displacements observed with phenanthrene are similar to those with C_6H_6. The first band is more markedly displaced towards the red in alcohols than in hexane and is therefore due to the 9 and 10 positions both of which are cationoid but weakened in comparison with anthracene, in consequence of their *o*-position to one another. The displacement of the limits of absorption by linear annelation of C_6H_6 nuclei is discussed. H. W.

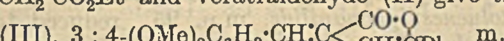


(I.)

Influence of solvent on the course of chemical reactions. VI. Bromination of aromatic compounds. K. Lauer and R. Oda (Ber., 1936, 69, [*B*], 978—985).—The bromination of $C_{10}H_8$ is accompanied by rapid diminution of the reaction const. In the cases of Me oleate and *cyclo*hexene halogenation proceeds rapidly at first but very slowly towards the end of the change; addition of unsaturated material immediately restores the rate. With $C_{10}H_8$ this is not the case so that the decay in rate is not attributable to the $C_{10}H_8$ mol. Retardation appears due to HBr and the production of polybromides which have no brominating action. The phenomena are complex. Similar retardation is caused by bromides and to a smaller extent by alkali chlorides but not by HCl. I accelerates greatly due to union with HBr. The bromination of C_6H_6, anthracene (I), phenanthrene, *lin.*-benzanthracene (II), 9-bromoanthracene, dihydroanthracene, *o*-xylene, and Ph_2 usually in hexane and (or) AcOH has been studied. The rate of bromination is dependent on the concn. due to the formation of polybromides and of associates of the aromatic mols. The aromatic hydrocarbons do not appear to be present in two forms one of which has a diradical nature; this is shown by the course of bromination after addition of fresh solution and by the observation that (II) is halogenated more slowly than (I). H. W.

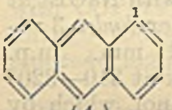
Fused carbon rings. XI. Action of aluminium chloride on decahydronaphthalene. R. L. Jones and R. P. Linstead (J.C.S., 1936, 616—621; cf. this vol., 713).—The low-boiling products of the action of $AlCl_3$ on decahydronaphthalene at 130° probably contain 1 : 4- (or, less probably, 2 : 5-) *dimethyl*-0 : 3 : 3-dicyclo*octane* (I); other fractions yield by dehydrogenation C_6H_6, PhMe, and mesitylene, proving the presence of *cyclo*hexane, methyl- and 1 : 3 : 5-trimethyl-*cyclo*hexane; formation of the last-mentioned product must have involved drastic degradation and resynthesis. A methylhydrindane may also have been present. (I), b.p. 158—163°, is stable to Br and $KMnO_4$, and hardly affected by Ni–Al dehydrogenating catalysts; it gives a (?1-)*Cl*-derivative, b.p. 88—91°/16 mm., and thence (NH_2Ph or *p*-NO_2·C_6H_4·CO_2Ag) 1 : 4-*dimethyl*-$\Delta^{\prime 1}$-0 : 3 : 3-dicyclo*octene* (II), b.p. 54—60°/20 mm., oxidised by $KMnO_4$ to ? 3-*acetyl*-1-*methyl*cyclo*pentane*-2-*acetic acid*, m.p. 120° (*semicarbazone*, m.p. 195°; gives CHI_3). The structure of (I) is not certain, but is probable from the above reactions and from correspondence of *n* and *d* for (I) and (II) with those of analogous compounds described below; the above compounds are probably *trans*. The Na derivative of Et 5-methyl*cyclo*pentanone-2-carboxylate (modified prep.; 70—80% yield) and CHMeBr·CO_2Et give *Et* 5-*methyl*cyclo*pentanone*-2-*carboxylate*-2-α-*propionate*, b.p. 171—175°/19 mm. (with some open-chain ester, b.p. 180—190°/20 mm.), which with hot HCl yields 5-*methyl*cyclo*pentanone*-2-α-*propionic acid*, m.p. 76° (*phenylhydrazone*, m.p. 192°), the *Et* ester, b.p. 127—128°/12 mm., of which could not be condensed with

$CN{\cdot}CH_2{\cdot}CO_2Et$. Et 4-methyl*cyclo*pentanone-2-carboxylate, b.p. 123—125°/24 mm., is obtained in 30% yield from 4-methyl*cyclo*hexanol by way of crude β-methyladipic acid and its Et ester, b.p. 138—144°/16—17 mm.; its Na derivative with $CH_2Cl{\cdot}CO_2Et$ affords *Et*$_2$ 4-*methyl*cyclo*pentanone-2-carboxylate-2-acetate* (65% yield), b.p. 180—183°/24 mm., converted by conc. HCl into *methyl*cyclo*pentanone-2-acetic acid* (crude), b.p. 183—190°/24 mm., the *Et ester*, b.p. 130—133°/23 mm. (*semicarbazone*, m.p. 141°), of which with $CN{\cdot}CHK{\cdot}CO_2Et$ affords *Et*$_2$ 4-*methyl*cyclo*pentylidene-1-cyanoacetate-2-acetate*, b.p. 194°/4 mm. (35% yield). Hydrogenation (Adams) in EtOH gives *Et*$_2$ 4-*methyl*cyclo*pentane-1-cyanoacetate-2-acetate*, b.p. 205°/17 mm., which with HCl affords 38% of 4-*methyl*cyclo*pentane-1 : 2-diacetic acid* (III), m.p. 173—174°, and a little 5-*methyl*-0 : 3 : 3-dicyclo*octan-2-one* (IV), b.p. 104°/26 mm. (*semicarbazone*, m.p. 183°), obtained in 32% yield from (III) and $Ba(OH)_2$ at 270—280°. (IV) and MgMeI give a carbinol, dehydrated by NH_2Ph,HBr to 2 : 5-*dimethyl*-Δ^1-0 : 3 : 3-dicyclo*octene* (70% yield), b. p. 167°, which is hydrogenated (Adams; no solvent) to 2 : 5-*dimethyl*-0 : 3 : 3-dicyclo*octane*, b.p. 165—167°. R. S. C.

Syntheses of 1-phenylnaphthalenes. W. N. Howell and A. Robertson (J.C.S., 1936, 587—589).—1-Keto-1 : 2 : 3 : 4-tetrahydronaphthalene and p-$OMe{\cdot}C_6H_4{\cdot}MgBr$ in Et_2O give 1-p-*anisyl*-3 : 4-*dihydronaphthalene*, b.p. 198—200°/12 mm., m.p. 76°, dehydrogenated by Se at 280—300° to 1-p-*anisylnaphthalene*, m.p. 116·5° (*NO_2*-derivative, m.p. 129°). 6 : 7-Dimethoxy-1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene and MgPhBr give similarly 6 : 7-*dimethoxy-1-phenyl*-3 : 4-*dihydronaphthalene*, b.p. 215—217°/14 mm., m.p. 68·5°, and 6 : 7-*dimethoxy-1-phenylnaphthalene* (I), m.p. 110°, and thence by HI–Ac_2O at 140—145° the (*OH*)$_2$-compound, m.p. 167—168°. Similar reactions give 7-*methoxy-1-phenyl*-, m.p. 42·5—43·5°, and 1-p-*anisyl-2-methyl*- (with *pp'*-dianisyl), m.p. 91—92°, -3 : 4-*dihydronaphthalene*, and 7-*methoxy-1-phenyl*-, m.p. 48—50°, b.p. 214—215°/19 mm., and 1-p-*anisyl-2-methyl-naphthalene*, m.p. 108°. The Na derivative of $CH_2Bz{\cdot}CH_2{\cdot}CO_2Et$ and veratraldehyde (II) give the *lactone* (III),  $3:4\text{-}(OMe)_2C_6H_3{\cdot}CH{:}C{<}\begin{matrix}CO{\cdot}O\\CH{:}CPh\end{matrix}$, m.p. 131°, converted by hot MeOH into *Me* β-*benzoyl*-α-*veratrylidenepropionate* (IV), m.p. 96°, and thence by cold NaOMe into the corresponding *acid*, m.p. 168°. (III) with I in $CHCl_3$ at room temp. (5 days) yields 6 : 7-*dimethoxy-1-phenylnaphthalene-3-carboxylic acid*, m.p. 265° [also obtained by boiling (III) or (IV) with HCl–MeOH and hydrolysing the resulting *Me* ester, m.p. 124°], which with Cu-bronze in boiling quinoline affords (I). The Na derivative of p-$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$ and PhCHO with Ac_2O at 100° yield the *lactone*, m.p. 174°, analogous to (II), and thence β-p-*anisoyl*-α-*benzylidenepropionic acid*, $+0{\cdot}5C_6H_6$, m.p. 170° (*Me* ester, m.p. 74—75°); none of these products could be cyclised. $(OMe)_3C_6H_2{\cdot}CO{\cdot}CHN_2$ and HCl–Et_2O at 0° give ω-*chloro*-3 : 4 : 5-*trimethoxyacetophenone*, m.p. 86—87°, giving with KOAc–EtOH and a trace of I the ω-*OAc*-derivative, m.p. 85—86°, and with $CHNa(CO_2Et)_2$ 3 : 4 : 5-*trimethoxybenzoylmalonic acid*, m.p. 167—168°, and thence (160°) 3 : 4 : 5-*trimethoxybenzoylpropionic acid* (V), dimorphic, m.p. 116° and 122°; the Na derivative of (V) with (IV) affords the γ-*lactone*, m.p. 172—173°, of β-3 : 4 : 5-*trimethoxybenzoyl*-α-*veratrylidenepropionic acid*. R. S. C.

Aromatic fluoro-compounds. XXI. "*ortho*-Effect" in the "2-fluoro-1-nitronaphthalene" of Willstaedt and Scheiber. G. Schiemann and E. Ley (Ber, 1936, 69, [*B*], 960—964; cf. A., 1935, 856).—Repetition of the work of Willstaedt *et al.* (A., 1934, 522) shows that diazotisation of 1 : 2-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$ in conc. HCl is accompanied by replacement of NO_2 by Cl. The "2-fluoro-1-nitronaphthalene" is therefore 1-*chloro-2-fluoronaphthalene*, m.p. 62·5°. The isolation of 2 : 1-$C_{10}H_6F{\cdot}NO_2$ from the products of the nitration of 2-$C_{10}H_7F$ is very difficult, but the crude product can be reduced by the usual methods. H. W.

Structure of anthracene. L. F. Fieser and W. C. Lothrop (J. Amer. Chem. Soc., 1936, 58, 749—753; cf. A., 1935, 1230).—Structure (*A*) (cf. Fries *et al.*, *ibid.*, 761) is indicated by the observation that 1 : 5-disubstituted-2 : 6-dihydroxyanthracenes do not couple with diazotised *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_3H$ or *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$. The position of equilibrium between the tautomeric forms of unsymmetrical derivatives (*e.g.*, 2-OH-, 2-NH_2-, 1-NO_2-, 1 : 2-benz-) can be inferred from oxidation–reduction potential data for quinones.



(*A*.)

6-Hydroxy-*o*-toluic acid (I) (from Na β-naphthylamine-4 : 8-disulphonate and 50% NaOH at 250—275°) is methylated (Me_2SO_4, alkali) to the 6-*OMe-acid*, m.p. 145—146°; the chloride, m.p. 40°, of this with $AlCl_3$ in CS_2 gives 4—10% of 2 : 6-*dimethoxy*- (II), m.p. about 305° (decomp.), and 3—7% of 2 : 6-*dihydroxy*-, decomp. about 330° (*diacetate*, m.p. 253°), -1 : 5-*dimethylanthraquinone*. Reduction of (II) with $SnCl_2$ and AcOH–conc. HCl affords the *hydroxyanthrone* (?), decomp. about 295°, which is further reduced (method: Hall and Perkin, J.C.S., 1923, **123**, 2029) to 2 : 6-*dimethoxy*-1 : 5-*dimethylanthracene*, m.p. 250° (decomp.), demethylated (48% HBr, AcOH) to 2 : 6-*dihydroxy*-1 : 5-*dimethylanthracene*, decomp. from about 340° [*diacetate*, m.p. 266° (decomp.)]. An anthraquinone could not be obtained from (I) and $ZnCl_2$ (cf. G.P. 87,620), H_2SO_4, H_2SO_4–B_2O_3, or P_2O_5. (I) and $SOCl_2$ in Et_2O give the *depside*, $OH{\cdot}C_6H_3Me{\cdot}CO_2{\cdot}C_6H_3Me{\cdot}OH$, m.p. 211°. 2 : 6-*Diallyloxyanthraquinone*, m.p. 149° [from the $(OH)_2$-derivative, allyl bromide, and K_2CO_3 in $COMe_2$], is reduced [as for (II)] to 2 : 6-*diallyloxyanthracene*, m.p. 201°, which when heated in $NPhEt_2$–Ac_2O and N_2 at 160—180° affords 2 : 6-*diacetoxy*-1 : 5-*diallylanthracene*, m.p. 179° [the 2 : 6-$(OH)_2$-derivative could not be obtained cryst.]. H. B.

Polycyclic aromatic hydrocarbons. XIV. Synthesis of 3 : 4-benzphenanthrene. C. L. Hewett (J.C.S., 1936, 596—599; cf. A., 1935, 1359).—A 7·3% over-all yield of 3 : 4-benzphenanthrene (I) is obtained from $CO_2H{\cdot}CH_2{\cdot}CH(CHPh_2){\cdot}CO_2H$ (II). Difficulty of ring-closure in the last stage indicates resistance to formation of ring-structure of

(I), possibly due to steric hindrance. (II) and AcCl give the anhydride, which (crude) with $AlCl_3$ in $PhNO_2$ at 0° gives 4-*keto*-1-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoic acid*, m.p. 208—209° (*Et* ester, m.p. 122—123°). Ordinary Clemmensen reduction gives poor yields, but reaction in boiling PhOMe and purification by way of the ester gives a 78% yield of 1-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoic acid*, m.p. 148—148·5°, b.p. 200°/0·8 mm.; the *Et* ester, b.p. 170—173°/0·8—1 mm., thereof with Na–EtOH gives 1-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthylcarbinol*, b.p. 175—180°/1 mm., m.p. 93—94°, and thence ($SOCl_2$) the *chloride*, m.p. 71—72°, b.p. 168°/0·8 mm.; the Grignard reagent with CO_2 affords 1-*phenyl*-1 : 2 : 3 : 4-*tetrahydronaphthyl*-2-*acetic acid* (III), m.p. 138—139° after sintering (*Et* ester, m.p. 55—56°), with a little 1-*phenyl*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 46—47°, and αβ-*bis*-(1-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthyl*)*ethane*, m.p. 169·5—170·5°. Cyclisation of (III) was effected only by the action of $AlCl_3$ in CS_2 on the *chloride* (obtained by $SOCl_2$) and yielded 2-*keto*-1 : 2 : 9 : 10 : 11 : 12-*hexahydro*-3 : 4-*benzphenanthrene* (IV), m.p. 154—155° (*oxime*, m.p. 191—192°), the *semicarbazone*, m.p. 235°, of which with NaOEt at 175—180° gives 1 : 2 : 9 : 10 : 11 : 12-*hexahydro*-3 : 4-*benzphenanthrene*, b.p. 148—153°/0·2 mm., m.p. 47·5—48°, dehydrogenated by Pd-black at 310—320° to (I). (IV) and MgMeI yield a carbinol, which by dehydration by $KHSO_4$ at 100° and dehydrogenation by Pd-black at 300—310° gives 2-*methyl*-3 : 4-*benzphenanthrene*, m.p. 69·5—70°. R. S. C.

Preparation of amino- and halogeno-phenanthrenes. W. E. BACHMANN and C. H. BOATNER (J. Amer. Chem. Soc., 1936, 58, 857—858).—Hydrolysis of the products obtained by Beckmann rearrangement of the oximes of 1-, m.p. 112—113°, 2-, 3-, and 9-acetylphenanthrenes gives 1-, m.p. 145—146°, 2-, 3-, and 9-aminophenanthrenes, respectively. The following have been prepared: 1-, m.p. 120—120·5°, 2-, m.p. 85·5—86°, and 3-, m.p. 80·5—81·5°, chloro-; 1-, m.p. 109·5—110°, 2-, m.p. 95—96°, and 3-, m.p. 83—84°, bromo-; 1-, m.p. 112·5—113°, 2-, m.p. 116—116·5°, and 3-, m.p. 83·5—84°, iodophenanthrene. H. B.

Diradical formula of rubenes. C. DUFRAISSE (J. Amer. Chem. Soc., 1936, 58, 858).—Schönberg's claim (this vol., 326) to priority is disputed. H. B.

[Reversible chemical absorption of free oxygen by organic compounds.] C. DUFRAISSE (Ber., 1936, 69, [*B*], 1228).—A reply to Schönberg (this vol., 600). H. W.

Catalytic condensation of acetylene with aromatic amines. I. Condensation of acetylene with aniline in presence of cuprous and cupric chlorides. N. S. KOZLOV and P. N. FEDOSEEV (J. Gen. Chem. Russ., 1936, 6, 250—258).—NH_2Ph and C_2H_2 in presence of $CuCl_2$ yield a product, from which quinaldine (I) and tetrahydroquinaldine (II) are obtained by distillation. In presence of excess of NH_2Ph *cis-trans*-NHPh·CHMe·CH:CH·NHPh (III), also affording (I) and (II) when heated, is obtained. In presence of CuCl the products isolated after 1—10 days were (I) (50% yield), (II), (III), and NHPhEt; $NPhEt_2$ and NHPhBu were not found. The process is represented: $2NH_2Ph+C_2H_2 \rightarrow CHMe(NHPh)_2$ (IV); 2(IV) → $2NH_2Ph+$(III); $NH_2Ph+C_2H_2 \rightarrow$ NPh:CHMe (V); 2(V) → (III) → (I)$+NH_2Ph+H_2$; (I)$+2H_2 \rightarrow$ (II). The catalytic action of CuCl and $CuCl_2$ appears to depend on formation of triple salts with NH_2Ph and C_2H_2. R. T.

Reactivity and structure of primary aromatic amines. G. VAVON and L. BOURGEOIS (Compt. rend., 1936, 202, 1446—1448).—CH_2PhBr and 2 : 4 : 6-$C_6H_2Me_3{\cdot}CH_2Br$ with aromatic amines afford derivatives, the times of half formation of which are measured by the HBr liberated. When no steric factors are involved, the less basic amines react more slowly. *o*-Derivatives react more slowly than *p*-, the dimensions of the *o*-substituent being the determining factor. J. L. D.

Rates of reaction and energies of activation of 1 : 2 : 4-chlorodinitrobenzene with aromatic primary amines.—See this vol., 802.

Stereochemistry of tervalent nitrogen compounds. I. Attempted resolution of substituted derivatives of aniline. E. V. MENON and D. H. PEACOCK (J. Indian Chem. Soc., 1936, 13, 104—108).—$NPhEt{\cdot}CH_2Ph$ and 20% oleum at 80° give sulphobenzylethylaniline, the *brucine* salt, m.p. 164—165°, of which (after 5 crystallisations) yields an inactive Na salt. N-*Benzyl*-p-*toluenesulphon*-m-*nitroanilide* (I), m.p. 118° [from *p*-toluenesulphon-*m*-nitroanilide (modified prep.) and CH_2PhCl in EtOH–NaOH], is reduced (Sn, conc. HCl, EtOH) to the -m-*aminoanilide*, m.p. 137° (*H tartrate*, m.p. 136°, $[\alpha]^{23}_{D}$ +4·57° in $COMe_2$; *γ-phenoxy-α-methylbutyryl* derivative, m.p. 117°), methylated (MeI, aq. Na_2CO_3) to the -m-*dimethylaminoanilide*, m.p. 101° (*methiodide*, m.p. 111—112°, which affords a non-cryst. product with Ag bromocamphorsulphonate). N-*Benzyl*-p-*toluenesulphon*-p-*nitroanilide*, m.p. 128° [obtained similarly to, but less readily than, (I)], is reduced to the -p-*aminoanilide*, m.p. 162° (*γ-phenoxy-α-methylbutyryl* derivative, m.p. 143°), which does not form a tartrate. The dry Na salt of *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NHPh$ and *m*-$NO_2{\cdot}C_6H_4{\cdot}CH_2Cl$ at 140—150° give N-m-*nitrobenzyl*-p-*toluenesulphonanilide*, m.p. 95°, reduced to N-m-*aminobenzyl*-p-*toluenesulphonanilide*, m.p. 129° (*H tartrate*, m.p. 133°, $[\alpha]^{28}_{D}$ +4·6° in $COMe_2$; *γ-phenoxy-α-methylbutyryl* derivative, m.p. 111°). None of the above NH_2-derivatives shows signs of dissymmetry. H. B.

Mesomeric effect of the dimethylamino-group in dimethylaniline, and the nature of its interaction with halogen groups. R. J. B. MARSDEN and L. E. SUTTON (J.C.S., 1936, 599—606).—The dipole moments of $NPhMe_2$ and its *p*-Me, -Cl-, -Br-, -I-, -NO_2-, and -NH_2-derivatives, measured in C_6H_6 solution at 25°, are 1·58, 1·29, 3·29, 3·37, 3·24, 6·87, and $1{\cdot}42\times10^{-18}$ e.s.u., respectively. On the assumption that the interaction between Me and NMe_2 is zero the mesomeric effect of the latter group is calc. to be 1·55, the angle between the moment of $NPhMe_2$ and the $C{\cdot}NMe_2$ linking being 38° (cf. 33·5°, the smaller of the two possible vals. obtained by Hertel *et al.*, this vol., 12). The interaction moment $\mu_{int.}$ (that moment parallel to the axis passing through the two substituent-bearing C atoms necessary to convert the calc. to the observed val.) between NMe_2 and substituent groups are calc. to be Cl 0·34, Br 0·46, I 0·69, and NO_2 1·86 : NMe_2 thus reduces the mesomeric effect of the halogens, suppressing it almost completely in the I-derivative : $\mu_{\mathrm{int.}}$ decreases in the order $\cdot NMe_2 > (\cdot NH_2, \cdot OPh, \cdot OMe) > \cdot OH$, and is always positive relatively to the main group for any of the substituent groups used (cf. also Bennett *et al.*, A., 1934, 831). The nature of mesomeric effects and their mutual interaction are fully discussed especially in relation to excited structures, the increase or decrease in the relative importance of which may be produced not only by similar or dissimilar requirements of valency arrangements of the two groups, but also by the fields of the groups, and an attempt to assess the relative importance of such "valency" and "polar" effects is made. J. W. B.

De-ethylation of diethylaniline. G. I. Gerschzon and G. Berenschtein (J. Appl. Chem. Russ., 1936, **9**, 496—501).—A mixture of NH_2Ph, NHPhEt, and $NPhEt_2$ is obtained by heating NH_2Ph and $NPhEt_2$ in presence of HCl or $C_6H_3Me(SO_3H)_2$. EtCl and C_2H_4 are obtained as by-products. R. T.

Catalytic synthesis of diphenylamine. G. I. Gerschzon and R. P. Lastovski (J. Appl. Chem. Russ., 1936, **9**, 502—504).—$NHPh_2$ is obtained in good yield from NH_2Ph,HCl (I) (2 mols.) and $AlCl_3$ (0·43 mol.) (220—240°; 20 hr.). The reaction is represented as $3NH_2Ph+AlCl_3 \rightarrow Al(NH_2PhCl)_3$ (II); (II)+3(I) $\rightarrow 3NHPh_2+3NH_4Cl+AlCl_3$. R. T.

Preparation of di-α-naphthylmethylamine. H. Rupe and W. Brentano (Helv. Chim. Acta, 1936, **19**, 581—588).—Hydrogenation (Ni) of α-$C_{10}H_7\cdot CN$ (I) in EtOH–EtOAc–H_2O at 75°/70 atm. gives 71·1% of $NH(CH_2\cdot C_{10}H_7\text{-}\alpha)_2$ (II) and 5% of α-$C_{10}H_7\cdot CH_2\cdot OH$, m.p. 59—60°. Mostly $NH_2\cdot CH_2\cdot C_{10}H_7\text{-}\alpha$ (III) is obtained at 75°/1 atm., room temp./75 atm., or room temp./1 atm. Other methods give poor yields of (II). 15 g. of α-$C_{10}H_7\cdot CH_2Cl$ (IV), m.p. 31—32°, b.p. 150—155°/10 mm. (modified prep. by CH_2O–HCl), and NH_3–EtOH at 160° give 5 g. of (III), 5·1 g. of (II), and 1·5 g. of *tri-(α-naphthylmethyl)amine*, m.p. 300° [*hydrochloride*, *nitrate*, *phosphate*, *sulphate*, and *acetate*, more sol. than the salts of (II)]. 10 g. of α-$C_{10}H_7\cdot CH_2Br$ (improved prep. by Br at 190° in ultra-violet light) and NH_3–EtOH at 100° give 1·5 g. of (II) and 4·8 g. of (III), at 150° 6 g. of (III). (I) (prep. by diazo-reaction with $K_2Ni(CN)_4$ in 75—78% yield), b.p. 147—148°/12 mm., and NH_3–H_2S–EtOH at 100° give a very poor yield of (III). *α-Naphthylmethylphthalimide*, m.p. 174—175°, with conc. HCl at 100° gives 86% of (III), 10 g. of which with (IV) give 1·8 g. of (II). (IV), p-$C_6H_4Me\cdot SO_2\cdot NH_2$, and hot KOH–EtOH give a good yield of p-*toluenesulphondi-(α-naphthylmethyl)amide*, m.p. 134° (obtained also in 50—55% yield by hot $NaOBu^a$–Bu^aOH), with conc. HCl at 100° gives a poor yield of (I). α-$C_{10}H_7\cdot CHO$ [prep. from (IV) by $(CH_2)_6N_4$ in 48% yield], b.p. 158—159°/14 mm., and (III) give *α-naphthylidene-α-naphthylmethylamine*, m.p. 105°, giving by hydrogenation (Ni) in EtOH–H_2O 10% of (II). R. S. C.

[Pharmacology of] quaternary ammonium iodides.—See this vol., 892.

Reduction of nitro-compounds by hydrazine. [Preparation of 4 : 4′-azoxyphenetole.] B. M. Bogoslovski (J. Appl. Chem. Russ., 1936, **9**, 725—727).—A 100% excess of N_2H_4,H_2O added to 4-nitrophenetole (I) in hot NaOEt–EtOH gives 4 : 4′-azoxyphenetole in 62% yield. With 4-nitrotoluene in place of (I), the chief product is an unidentified substance, m.p. 265°, together with some 4 : 4′-azoxytoluene. R. T.

Action of Grignard compounds on phenylhydrazones. Preparation of *s*-alkylphenylhydrazines. P. Grammaticakis (Compt. rend., 1936, **202**, 1289—1291).—Contrary to Busch *et al.* (A., 1905, i, 519) arylphenylhydrazones react with MgRX: $CHAr{:}N\cdot NHPh+MgRX \rightarrow CHRAr\cdot NH\cdot NHPh$. Thus $CHPh{:}N\cdot NHPh$ and MgEtBr give s-*phenyl-α-phenyl*-n-*propylhydrazine* (I), b.p. 210°/15 mm. [*hydrochloride*, m.p. 217° (decomp.); Ac_1 derivative, m.p. 138°; *phenylurethane*, m.p. 140°], reduced by Zn–AcOH quantitatively to NH_2Ph and $NH_2\cdot CHPhEt$, which, with $COPhPr^a$, are also obtained as secondary products in the formation of (I). (I) has the usual basic and reducing properties of *s*-alkylphenylhydrazines. J. W. B.

Velocity of diazotisation.—See this vol., 802.

Mechanism of diazotisation. J. Böeseken and H. Schoutissen (Rec. trav. chim., 1935, **54**, 956—958).—The conclusions of Reilly *et al.* (A., 1935, 1232), who have overlooked previous work by the authors and others, are criticised. Attention is drawn to the conclusion of Schoutissen (A., 1934, 67) that substituents in the C_6H_6 nucleus exert a twofold opposing influence on the velocity of diazotisation, by affecting the basicity of the amine and the rate of transformation of the NH_2-group. H. G. M.

Double salts of aryldiazonium chlorides with heavy-metal chlorides. K. A. Kotscheschkov and A. N. Nesmejanov (J. Gen. Chem. Russ., 1936, **6**, 144—160).—128 double salts of *o*-, *m*-, and *p*-$R\cdot C_6H_4\cdot N_2Cl$ (R = H, Cl, Br, I, NO_2, Me, OMe, OH) with $ZnCl_2$, $CdCl_2$, $TlCl_3$, $SnCl_4$, $PbCl_4$, $BiCl_3$, $AuCl_3$, $PtCl_4$, and $FeCl_3$ are described. R. T.

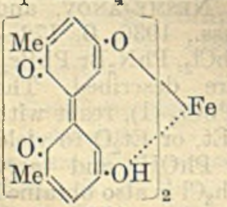
Double salts of lead halides and benzenediazonium halides, and their decomposition. K. A. Kotscheschkov, A. N. Nesmejanov, and N. K. Gipp (J. Gen. Chem. Russ., 1936, **6**, 172—175).—The double salts $PhN_2Cl,PbCl_2$, $PhN_2Br,PbBr_2$, and p-$NO_2\cdot C_6H_4\cdot N_2Br,PbBr_2$ are described. The above salts, as well as $2PhN_2Cl,PbCl_4$ (I), react with Zn or Cu in boiling $COMe_2$, AcOEt, or Et_2O to yield C_6H_6, Ph_2 or $(C_6H_4R\cdot)_2$, PhX, PhOH, and tarry products; in the case of (I), $PbPh_3Cl$ is also obtained in small yield. R. T.

Nature of the reaction between diazotised sulphanilic acid and proteins. H. Eagle and P. Vickers (J. Biol. Chem., 1936, **114**, 193—197).—p-$SO_3Na\cdot C_6H_4\cdot N_2Cl$ (I) at p_H 7·2—7·6 is inactivated by glycine, alanine, lysine, ornithine, phenylalanine, proline, hydroxyproline, and indole, but not by diketopiperazine, NH_2Ac, or arginine. Each NH_2

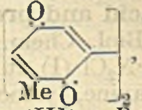
inactivates about 2 mols. of (I). This explains why proteins commonly inactivate more (I) than can be accounted for by the histidine- and tyrosine-Ph components, since free NH_2 and NH and indole groups also react. R. S. C.

Condensation of oximes with aromatic diazo-compounds. A. Mangini (Atti R. Accad. Lincei, 1935, [vi], **22**, 452—457).—Structures proposed for these compounds (cf. A., 1892, 163, 1079; 1906, i, 421; 1907, i, 567) are examined. The products from acetoxime and *p*-toluene- and *p*-nitrobenzene-diazo-compounds are hydrolysed by acid to $COMe_2$, *p*-toluidine or *p*-nitroaniline, and *p*-toluene- or *p*-nitrobenzene-diazoimide. The *p*-toluene compound with BzCl or $C_6H_4Br{\cdot}COCl$ yields benz- or bromobenz-*p*-toluidide, and with PhNCO yields *N*-phenyl-*N'*-*p*-tolylcarbamide. The *p*-nitrobenzene compound with PhNCO gives the same product as the latter and acetoxime, viz., $CMe_2{:}N{\cdot}O{\cdot}CO{\cdot}NHPh$. These reactions are in agreement with Bamberger's formulæ (A., 1899, i, 589), viz., $CMe_2{:}N{\cdot}O{\cdot}CMe_2{\cdot}N(OH){\cdot}N{:}N{\cdot}C_6H_4X$ ($X=p$-Me or p-NO_2), if the tautomeric formula ${\cdot}N(O){:}N{\cdot}NH{\cdot}$ is also admitted. Acetoxime Me ether and *p*-toluenediazo-compounds do not give $CMe_2(OH){\cdot}N(OMe){\cdot}N_2R$, but only *p*-toluenediazo-*p*-cresol. E. W. W.

Aliphatic diazo-compounds. II. Phenyl-α-naphthyldiazomethane. G. C. Harrold and M. G. Hemphill [with F. E. Ray] (J. Amer. Chem. Soc., 1936, **58**, 747—749).—*dl*-Phenyl-α-naphthylmethylamine, prepared by reduction of Ph α-$C_{10}H_7$ ketoxime (modified prep.), is resolved by *d*-camphorsulphonic acid (cf. Berlingozzi, A., 1920, i, 480) into the *l*-form, $[\alpha]_D^{22}$ −56·8° in Et_2O, which with $ClCO_2Et$ in Et_2O+5% NaOH gives *Et phenyl-α-naphthylmethylcarbamate*, m.p. 125°, $[\alpha]_D^{20}$ −28° in EtOH. The *NO*-derivative, m.p. 87—89° (decomp.), $[\alpha]_D^{25}$ +9·2° in EtOH, of this with KOMe in $COMe_2$ at −20° affords inactive *phenyl-α-naphthyldiazomethane* (I), m.p. 58° (decomp.), together with an active by-product. The inactivity of (I) may be due to its rapid racemisation or to the symmetrical structure of the diazo-group. H. B.



(II.)

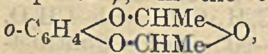
Reaction between cresols and hydrogen peroxide in presence of ferrous sulphate. K. Ono and T. Oyamada (Bull. Chem. Soc. Japan, 1936, **11**, 132—137).—Oxidation of *o*-cresol with 2% H_2O_2–aq. $FeSO_4$ under various conditions affords *p*-toluquinol (I) [$1{:}2{:}5$-$C_6H_3Me(OH)_2$] and a black substance, separated into Et_2O-sol. (*A*) and Et_2O-insol. (*B*) portions. Fractional pptn. of *A* with ligroin affords an insol. *substance* (II) $C_{28}H_{22}O_8Fe$, reduced by Zn–EtOH–HCl to 2 : 5 : 2′ : 5′-*tetrahydroxydi*-m-*tolyl*, m.p. 202° [converted into the known Ac_4 derivative (III), m.p. 135°], and, from the mother-liquor, ditolyldiquinone , converted by reduction-acetylation into (III). *B* is a black *substance*, (?) $C_{28}H_{22}O_8Fe$, possibly identical with the complex of Majima *et al.* (A., 1920, i, 837), converted in small yield by Zn–Ac_2O–NaOAc into an acetate, m.p. 193—195°, probably 4 : 4′ : 5 : 5′-tetra-acetoxydi-*m*-tolyl. Oxidation of *m*- and *p*-cresol gives (I) (only from *m*-) and similar black substances containing Fe not definitely identified. J. W. B.

Mobility of the nitro-group. I. Nitro-group mobility in 3 : 4-dinitroanisole. II. Preparation of 3 : 4-dinitroanisole. K. S. Toptschiev (Compt. rend. Acad. Sci. U.R.S.S., 1935, **4**, 201—204, 204—106).—I. 3 : 4-Dinitroanisole when heated (140—150°; 8 hr.) with δ-amino-α-diethylaminopentane gives δ-(2-*nitro-5-methoxyanilino*)-α-*diethylaminopentane*, b.p. 205°/2 mm. The constitution of this was confirmed by reduction ($SnCl_2$–HCl) to the corresponding 2-NH_2-compound, b.p. 190—192°/3 mm., which when heated with H_3AsO_4, glycerol, and H_2SO_4 (Skraup) gives 8-diethylamino-6-hydroxy-*sec.*-amylaminoquinoline, also obtained when the corresponding 6-OMe-derivative is heated with HCl (sealed vessel) (cf. lit.).

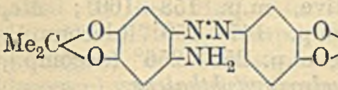
II. Nitration of $1{:}4$-$OMe{\cdot}C_6H_4{\cdot}NHAc$ gives the 3-NO_2-derivative, which when successively hydrolysed, diazotised in presence of excess of H_2SO_4, and then treated with $CuSO_3,Cu_2SO_3$ (cf. "Abegg's Handbuch, Kupfer," p. 462)–$NaNO_2$–H_2O gives 3 : 4-dinitroanisole in good yield. H. G. M.

Condensation of polyhydric phenols with acetone. C. H. Fisher, R. W. Furlong, and M. Grant (J. Amer. Chem. Soc., 1936, **58**, 820—822).—In agreement with Baker (A., 1935, 80), the compound obtained from o-$C_6H_4(OH)_2$ and $COMe_2$ (method: *loc. cit.*) is considered to be 5 : 6 : 5′ : 6′-tetrahydroxy-3 : 3 : 3′ : 3′-tetramethylbis-1 : 1′-*spiro*hydrindene (I). Guaiacol and $COMe_2$ similarly yield the 6 : 6′-dihydroxy-5 : 5′-dimethoxy-derivative, m.p. 266—267°, methylated (Me_2SO_4, 20% KOH) to the Me_4 ether (II), m.p. 155—156°, of (I). (II) could not be oxidised (CrO_3, AcOH). $1{:}2{:}4$-$C_6H_3(OAc)_3$ and $COMe_2$ or phorone in AcOH–conc. HCl give 4 : 6 : 7 : 4′ : 6′ : 7′-hexahydroxy-3 : 3 : 3′ : 3′-tetramethylbis-1 : 1′-*spiro*hydrindene, m.p. 265—267° (decomp.). Oily products were obtained from $COMe_2$ and quinol or toluquinol. H. B.

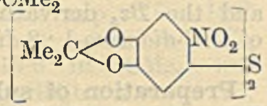
Cyclic ethers by condensation of pyrocatechol with aldehydes and ketones. G. Sloof (Rec. trav. chim., 1935, **54**, 995—1010).—Pyrocatechol (I) with $COMe_2$–P_2O_5 gives iso*propylidenepyrocatechol* (II), b.p. 182°/760 mm. [4-NO_2-, m.p. 92°, 4 : 5-$(NO_2)_2$- (III), m.p. 161°, 4-*Cl*-, b.p. 223°/760 mm., 4 : 5-Cl_2-, m.p. 88°, 4-*Br*-, m.p. 12°, b.p. 122°/20 mm., 4 : 5-Br_2-, m.p. 92°, b.p. 166°/20 mm., 4-*chloro-5-bromo*-, m.p. 78°, 4-NH_2- (IV), m.p. 35°, b.p. 135°/11 mm., 4-*I*-, m.p. 47°, b.p. 130°/12 mm., 4-*chloro-5-nitro*-, m.p. 118°, 4-*bromo-5-nitro*-, m.p. 130°, 4-*iodo-5-nitro*-, m.p. 114°, derivatives). 4-*Chloro-5-bromo*-, m.p. 90° (Ac_2 derivative, m.p. 104°), 4-*chloro-5-nitro*-, m.p. 169° (Ac_2 derivative, m.p. 119°), and 4-*bromo-5-nitro*-, m.p. 172° (Ac_2 derivative, m.p. 122°), -*pyrocatechol* are described. Diazotised (IV) couples with (IV) giving the red-brown *compound* (V), m.p. 179°, from which the $:CMe_2$ is readily hydrolysed by H_2SO_4. (III) with a little NH_3–H_2O–H_2S–EtOH gives the *sulphide* (VI), m.p. 230°, with more of this reagent gives the corresponding *disulphide*, m.p. 247° (decomp.), and with excess gives 5-*nitro*-4-*aminopyrocatechol*, m.p. 127°. The condensation *products* of (I) with the following ketones are described (b.p./20 mm. are given in parenthesis): COMeEt (94°); $COMePr^{\alpha}$ (107°); $COMeBu^{\beta}$ (114·5°); $COMe\cdot C_9H_{19}$ (118°); $COEt_2$ (105°); $COEtPr^{\alpha}$ (121°); $COPr^{\alpha}_2$ (131·5°); $CH_2Ac\cdot CO_2Et$ (155°); *cyclo*pentanone (124°); and *cyclo*hexanone (141°). Hydrolysis of the product from (I) and $CH_2Ac\cdot CO_2Et$ gives an *acid*, m.p. 61° [the 4-NO_2-derivative (VII), m.p. 125°, crystallises from PhMe and $CHCl_3$ with 1 mol. of solvent and has m.p. 41° from $CHCl_3$], decomposed by heat into (II). (VII) is resolved by cinchonine and then has m.p. 117·5°, $[\alpha]^{15}$ +41·0° in EtOH (*cinchonine* salt of the d-*acid* has [α] +167°). The *Et* ester (VIII), m.p. 71°, of (VII) with KOH–EtOH at room temp. gives *Et* β-(2-*hydroxy*-5-*nitrophenoxy*)*crotonate* (IX), m.p. 127° (*Ac* derivative, m.p. 59°; *Me ether*, m.p. 120°), as the *K* salt, which when heated passes irreversibly into a second *form* which yields an *isomeride* of (IX), m.p. 137° [*Ac* derivative, m.p. 67°; *Me ether* (X), m.p. 106°]. (IX) and its isomeride are converted by heat into (VIII), and with Ag_2O–MeI give the same ether (X); this change of configuration is avoided by the use of CH_2N_2. With H_2SO_4 both the foregoing Me ethers give the same nitroguaiacol. (VIII) when boiled (1 hr.) with KOH–EtOH gives a mixture of the two forms of β-(2-*hydroxy*-5-*nitrophenoxy*)*crotonic acid*, decomp. 167° and 170°, respectively (corresponding *Me*$_2$ derivatives, m.p. 92° and 130°, obtained with CH_2N_2; Ag_2O–MeI gives the latter derivative with both acids); the former acid is less sol. than the latter in EtOAc. The two forms of the foregoing compounds are *cis–trans*-isomerides. (I) when heated with MeCHO and P_2O_5 gives a little *ethylidenepyrocatechol*, b.p. 75—79°/20 mm. (4-NO_2-derivative, m.p. 82°); in the cold, however, the *compound*



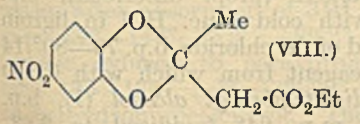
$o\text{-}C_6H_4{<}{\begin{matrix}O\cdot CHMe\\O\cdot CHMe\end{matrix}}{>}O$, m.p. 34°, b.p. 118°/20 mm. (4-NO_2-derivative, m.p. 111—112°), is formed. Only resins were obtained from (I) and CH_2O. The equilibrium const. for the reaction (I)+$COMe_2 \rightleftharpoons$ cyclic acetal+H_2O is ±0·001, and is much < would be expected from the parallelism between this quantity for other diols and the formation of boric acid complexes. A stereochemical explanation for this divergence is given. H. G. M.



(V.)



(VI.)



(VIII.)

Synthesis of vanillin from cresols. I. Synthesis of homopyrocatechol. K. Ono and M. Imoto (Bull. Chem. Soc. Japan, 1936, **11**, 127—131).—Rearrangement of *m*- and *p*-$C_6H_4Me\cdot OAc$ with $AlCl_3$ at 130—160° gives, respectively, 2-hydroxy-4-methyl- and 6-hydroxy-3-methyl-acetophenone, both oxidised by 3% H_2O_2–NaOH at room temp. to homopyrocatechol [1 : 3 : 4-$C_6H_3Me(OH)_2$] [Ac_2 derivative, m.p. 57—58°, oxidised by 0·5*N*-H_2SO_4–2% $KMnO_4$ to 1 : 3 : 4-$CO_2H\cdot C_6H_4(OAc)_2$], methylation of which gives homoveratrole and creosol, oxidised by EtO·NO to veratric acid and vanillin, respectively. *o*-$C_6H_4Me\cdot OAc$ rearranges to 2-hydroxy-3-methylacetophenone, which gives no definite product by Dakin's oxidation. J. W. B.

Synthesis of 4-hydroxy-3-ethoxy-1-allylbenzene from 4-hydroxy-3-methoxy-1-allylbenzene (eugenol). N. Hirao (Bull. Chem. Soc. Japan, 1936, **11**, 179—184).—Eugenol Me ether and MgMeI in xylene at 160—180° give chavibetol (I) and eugenol, separated by fractional crystallisation of their benzoates and isomerised (KOH at 220°) to *iso*chavibetol (II) [1 : 3 : 4-$CHMe{:}CH\cdot C_6H_3(OH)\cdot OMe$]. *iso*Eugenol Me ether similarly gives *iso*eugenol and (I); eugenol and *iso*eugenol Et ether give, respectively safro- and *iso*safro-eugenol. (II) with $KEtSO_4$–KOH at 150—160° gives its Et ether, converted by MgMeI into *iso*homogenol [1 : 3 : 4-$CHMe{:}CH\cdot C_6H_3(OEt)\cdot OH$] (III). Chavibetol with EtBr–KOH at 80—90° gives its *Et ether*, b.p. 114°/6·5 mm. (oxidised to 4-methoxy-3-ethoxyallylbenzoic acid), converted by MgMeI into 4-*hydroxy*-3-*ethoxyallylbenzene* (*homogenol*), b.p. 112°/6·5 mm. (*phenylurethane*, m.p. 93·5—94·5°; *benzoate*, m.p. 45·5°), which is isomerised (KOH at 170—220°) to (III). J. W. B.

Raman spectra and decomposition reactions of ozonides; ozonides of *iso*eugenol methyl ether, eugenol methyl and ethyl ether, ethyl maleate and fumarate. E. Briner, E. Perrottet, H. Paillard, and B. Susz (Helv. Chim. Acta, 1936, **19**, 558—568).—When a substance is ozonised, the O_3 absorbed (taking account of a blank on the solvent) gives the max. (*a*), and determination of a product gives the min. (*b*) amount of ozonide formed. *iso*Eugenol Me ether gives (*a*) 45, (*b*) 38%, eugenol Me and Et ethers (*a*) 30 and 47, (*b*) 20 and 38%, respectively, of ozonide, (*b*) being determined by yields of aldehyde. Et_2 maleate and fumarate give (*a*) 31 and 33, (*b*) 30 and 27%, respectively, (*b*) being determined by yields of $Et_2C_2O_4$; Et_2 maleate reacts very slowly, Et_2 fumarate very quickly. The eugenol and *iso*eugenol ether ozonides retain the Raman spectra of the Ph but have lost those of the unsaturated side-chain which are replaced by new bands characteristic of the ozonide linking. The ozonides of Et_2 maleate and fumarate differ from those of the esters themselves only by an additional new band at 1821 $cm.^{-1}$ R. S. C.

Raman spectra of compounds belonging to the anethole, safrole, and eugenol groups.—See this vol., 777.

Condensation of ethylene chlorohydrin with resorcinol. D. C. Motwani and T. S. Wheeler (J. Univ. Bombay, 1935, **4**, Part II, 104—105).—*m*-$C_6H_4(OH)_2$, $CH_2Cl\cdot CH_2\cdot OH$, and 40% KOH at 100° give, according to the relative amounts, *resorcinol* β-*hydroxyethyl*, b.p. 185—195°/10 mm. (*diacetate*, m.p. 75°; *dibenzoate*, m.p. 90—91°), or *di*-β-*hydroxyethyl ether*, m.p. 95—96° (*diacetate*, m.p. 75—76°; *dibenzoate*, m.p. 110°). The ethers with

PCl_5 afford m-*chlorophenyl* β-*hydroxyethyl ether*, m.p. 78—79°, and *resorcinol di*-β-*chloroethyl ether*, m.p. 63—64°, b.p. 130—150°/1 mm. R. S. C.

C-Alkylresorcinols. I. 4 : 6-Diethylresorcinol and its reactions. R. C. Shah and P. R. Mehta (J. Univ. Bombay, 1935, **4**, Part II, 109—113).—5-Ethylresacetophenone (prep. by the Nencki–Sieber and Hoesch methods), m.p. 118—119° (Bz_2, m.p. 91—92°, 3-*Br*-, m.p. 123—125°, and 3 : *x* : *x*-Br_3-derivative, m.p. 144—145°; *phenylhydrazone, m.p.* 232—233°; *oxime*, m.p. 141—143°; *semicarbazone*, m.p. 300—302°), is reduced (activated Zn–Hg; HCl) to 4 : 6-diethylresorcinol, unstable, b. p. 150—151°/7 mm., m.p. 65—67° after softening at 55° (*di*-p-*nitrobenzoate*, m.p. 163—165°; CO_2Me-derivative, m.p. 83—85°), which with PhN_2Cl gives the 2-*benzeneazo*-compound, m.p. 89°, with $Hg(OAc)_2$ in EtOH yields the 2-*acetoxymercuri*-derivative, decomp. 200°, with 40% CH_2O and 2*N*-HCl gives *di*-(2 : 6-*dihydroxy*-3 : 5-*diethylphenyl*)*methane*, m.p. 119°, and with H_2SO_4 and malic acid or $CH_2Ac·CO_2Et$ affords 5-*hydroxy*-6 : 8-*diethyl*-, m.p. 148—149°, or 5-*hydroxy*-4-*methyl*-6 : 8-*diethyl-coumarin*, m.p. 169—170°, respectively. R. S. C.

Mechanism of formation of benzaldehyde-resorcinol resins. E. Mertens and M. Fonteyn (Bull. Soc. chim. Belg., 1936, **45**, 186—188).—Equimol. amounts of PhCHO and m-$C_6H_4(OH)_2$ in 0·5% NaOH–EtOH at 100° in an inert atm. gives 2 : 4-dihydroxydiphenylcarbinol (cf. J.C.S., 1910, **97**, 78), which with PhCHO in 10% NaOH–EtOH affords the same resin as is obtained from m-$C_6H_4(OH)_2$ and excess of PhCHO. J. L. D.

Nitration of 1 : 8-dihydroxynaphthalene. F. Calvet and (in part) (Miss) M. C. Carnero (J.C.S., 1936, 556—560).—With HNO_3 (*d* 1·4) at 25—30° 1 : 8-$C_{10}H_6(OAc)_2$ gives the 8-O-*Ac* derivative, m.p. 200° (decomp.) [*Me ether* (I), m.p. 115—117°], of 2 : 4-*dinitro*-1 : 8-*dihydroxynaphthalene* (II), m.p. 180—182° [Me_2 *ether* (III), m.p. 137—139°], obtained as its *K* salt (IV) by KOH–MeOH hydrolysis. Hydrolysis of (I) with cold KOH–MeOH affords some (IV) and 2 : 4-*dinitro*-8-*hydroxy*-1-*methoxynaphthalene*, m.p. 170—171°, hydrolysed to (II). Hydrolysis of (III) with boiling 2*N*-NaOH affords 2 : 4-*dinitro*-1-*hydroxy*-8-*methoxynaphthalene*, m.p. 179—180° (decomp.), reduced (Sn–HCl) to the *dihydrochloride* of the 2 : 4-$(NH_2)_2$-derivative, oxidised by HNO_3 to 3-methoxyphthalic acid. Similar reduction of (II) affords the *dihydrochloride* of 2 : 4-*diamino*-1 : 8-*dihydroxynaphthalene* [Bz_4 derivative, m.p. 257—258° (decomp.)]. Nitration of 1 : 8-methylenedioxynaphthalene with AcOH–HNO_3 (*d* 1·5) affords its (?) 2 : 7- (V), m.p. 198—200°, and 4 : 5-$(NO_2)_2$-derivative (VI), m.p. 177—179°. Hydrolysis of (V) with boiling 2*N*-NaOH affords (?) 2 : 7-*dinitro*-1 : 8-*dihydroxynaphthalene* (VII) $+H_2O$ and anhyd., m.p. 171—173° (decomp.) [Ac_1, m.p. 125—170° (decomp.) and Ac_2 derivative, m.p. about 228° (decomp.); Me_2 *ether*, m.p. 268—270° (decomp.)]. With boiling KOH–MeOH (V) gives (?) 2 : 7-*dinitro*-1-*hydroxy*-8-*methoxynaphthalene*, m.p. 218—220° (*Ac* derivative, m.p. 183—185°). Reduction of (VII) gives the *hydrochloride* of the 2 : 7-$(NH_2)_2$-derivative [Bz_4 derivative, m.p. about 300° (decomp.)]. By similar methods (VI) affords 4 : 5-*dinitro*-1 : 8-*dihydroxynaphthalene*, m.p. about 225° (decomp.) [Ac_2 derivative, m.p. 158—160°; Me_2 *ether*, darkens 140°, m.p. 147—150° (decomp.)], and the Bz_4 derivative, m.p. 255—256° (decomp.), of 4 : 5-*diamino*-1 : 8-*dihydroxynaphthalene*. J. W. B.

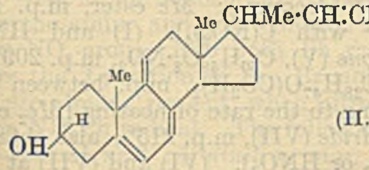
Preparation of substituted benzene-o-dithiols for use as specific reagents for tin. R. E. D. Clark (Tech. Publ. Internat. Tin Res. and Dev. Counc., 1936, *A*, No. 41, 7 pp.).—The prep. of toluene- and 1-chlorobenzene-3 : 4-dithiol is described. These reagents give an intense red coloration with Sn^{II} salts. E. S. H.

Synthesis of 2 : 3-di- and 2 : 3 : 4-tri-methylbenzyl alcohol. Anomalous reactions. T. Reichstein, A. Cohen, M. Ruth, and H. F. Meldahl (Helv. Chim. Acta, 1936, **19**, 412—418).—Reaction of $MgCl·CH_2R$ ($R=Ph$, C_6H_4Me, or $C_6H_3Me_2$) with CH_2O results in introduction of o-$CH_2·OH$ with reduction of the original CH_2Cl to Me (cf. A., 1903, i, 48). o-$C_6H_4Me·CH_2·OH$ (prep. described), b.p. 115—120°/14 mm., with cold conc. HCl in ligroin gives an 85—92% yield of the chloride, b.p. 76—80°/14 mm., the Grignard reagent from which with CH_2O gives 50% of 2 : 3-*dimethylbenzyl alcohol* (I), b.p. about 125°/12 mm., m.p. 64° (oxidised to 2 : 3-$C_6H_3Me_2·CO_2H$), and $(o$-$C_6H_4Me·CH_2)_2$, b.p. about 170—180°/12 mm., m.p. 65°. (I) gives similarly a 90% yield of the *chloride*, b.p. 99°/12 mm., and thence a poor yield of 2 : 3 : 4-*trimethylbenzyl alcohol*, m.p. 49—50° (*H phthalate*; oxidised to 2 : 3 : 4-$C_6H_2Me_3·CO_2H$), and probably 2 : 2′ : 3 : 3′-*tetramethyldibenzyl*, m.p. 111—112°, and 1 : 2 : 3-$C_6H_3Me_3$. R. S. C.

Reduction of γ-phenyl-α-methylallyl alcohol with deuterium. J. B. M. Coppock and S. M. Partridge (Nature, 1936, **137**, 907).—There is no change in b.p., μ, or optical rotatory power in the reduction products of this alcohol with H_2 and D_2. The results indicate that an asymmetric system of the type CHDRR′ has no optical rotatory power, and that the electrical fields associated with H and D in combination with C are approx. equiv. L. S. T.

Synthesis of 3-nitro-4-methoxybenzyl alcohol and of its alkyl ethers. R. Quelet and (Mlle.) Y. Germain (Compt. rend., 1936, **202**, 1442—1444; cf. A., 1921, i, 23).—o-$NO_2·C_6H_4·OMe$ with CH_2O, $ZnCl_2$, and HCl (gas) at 80—90° affords 3-nitro-4-methoxybenzyl chloride (I), m.p. 85·5—86° (free from 3 : 3′-dinitro-4 : 4′-dimethoxyphenylmethane; cf. A., 1934, 999), which when boiled with aq. NaOAc gives 3-*nitro*-4-*methoxybenzyl acetate*, m.p. 37°, hydrolysed (KOH) to 3-nitro-4-methoxybenzyl alcohol (*phenylurethane*, m.p. 129°), which with $KMnO_4$ gives 3-nitro-4-methoxybenzoic acid. (I) reacts with Na alkoxides to give ethers. The following are prepared: 3-*nitro*-4-*methoxybenzyl Me*, m.p. 30°, *Et*, b.p. 181°/16 mm., and Pr^a *ether*, b.p. 190°/15 mm. (decomp.). J. L. D.

Lumisterol. K. Dimroth (Ber., 1936, **69**, [*B*], 1123—1129).—Lumisteryl acetate with BzO_2H in $CHCl_3$ gives the corresponding *oxide* (I), $C_{30}H_{46}O_3$, m.p. 133°, $[\alpha]_D^{20}$ +119·2° in $COMe_2$, hydrolysed by cautious treatment with KOH–MeOH to *lumisterol oxide*, m.p. 132°, $[\alpha]_D^{21}$ +173° in $CHCl_3$. (I) is converted by hot H_2O into *lumistadienetriol acetate*, m.p. 178—179° (decomp.), $[\alpha]_D^{21}$ +27·8° in $CHCl_3$, hydrolysed to *lumistadienetriol*, m.p. 180—183° (decomp.) when rapidly heated, $[\alpha]_D^{21}$ +37·9° in $CHCl_3$ (*diacetate*, m.p. 143°, $[\alpha]_D^{20}$ +113·6° in $COMe_2$), isomeric with the compounds of Heilbron *et al.* (A., 1935, 1493). Lumisterol has thus the same structural formula as ergosterol; in the initial stages, therefore, irradiation causes only steric transformations, probably at $C_{(9)}$ or $C_{(10)}$. Dehydrolumisterol (Heilbron, *loc. cit.*) has the same absorption spectrum as dehydroergosterol and hence is probably (II). Catalytic hydrogenation of its acetate (III) (Pt in AcOH) ceases after absorption of $3H_2$ and yields a *product*, m.p. 142—143°, $[\alpha]_D^{19}$ −69·2° in $CHCl_3$, which is further reduced to perhydropyrocalciferyl acetate, m.p. 135—136°, $[\alpha]_D^{20}$ +26·38° in $CHCl_3$, hydrolysed to perhydropyrocalciferol. The identity of the products proves that no further steric transformations in other parts of the mol. occur during the conversion of lumisterol into tachysterol and vitamin-*D*. Ultraviolet light causes primarily fission between $C_{(9)}$ and $C_{(10)}$ and subsequently a displacement of the double linkings. Exposure to sunlight of (III) and eosin in EtOH affords a *compound* $C_{60}H_{86}O_4$, m.p. 183—184°. H. W.



(II.)

Synthesis of sterols with modified side-chains and their *epi*-derivatives from lithocholic acid. F. Reindel and K. Niederländer (Annalen, 1936, **522**, 218—239).—Nor*epi*coprostane-3 : 24-diol (I) (A., 1935, 1494) is converted by boiling Ac_2O into nor*epi*-Δ^{24}-coprostenyl acetate (II) (not characterised), which is reduced (H_2, PtO_2, AcOH) to nor*epi*coprostanyl acetate (+H_2O) (III), m.p. 83—84° (cf. Ruzicka and Goldberg, *ibid.*, 749). Energetic hydrolysis (5% EtOH–NaOH) of (III) affords nor*epi*coprostanol (IV), m.p. 147—148° (cf. *loc. cit.*), whilst mild hydrolysis (0·1% MeOH–NaOH) gives a 1 : 1-*compound* (+$2H_2O$), m.p. 110—112°, of (III) and (IV). Oxidation [CrO_3 (≡6O), AcOH] of (II) yields the *Ac* derivative (V), m.p. 145—146°, of *norlithocholyl Me ketone* (VI), m.p. 157—158° [*semicarbazone*, m.p. 226—227° (decomp.)]. Reduction (as above) of (V) affords the *Ac* derivative, m.p. 91—92°, of *norlithocholylmethylcarbinol* (+0·5H_2O), m.p. 155—157°, also formed by Wolff–Kishner reduction of (V) [as *semicarbazone*, m.p. 217—218° (decomp.)]. (IV) is oxidised (CrO_3, AcOH) to norcoprostan-3-one [semicarbazone, m.p. 167—168° (decomp.)], reduced (H_2, PtO_2, AcOH–conc. HCl) to *norcoprostan*-3-*ol* (VII), m.p. 117—118° (*acetate*, m.p. 122—123°), which is pptd. by digitonin. Similar reduction of norcoprostan-3-one-24-ol, m.p. 80—81° [semicarbazone, m.p. 168—169° (decomp.)] [from (I) and CrO_3–AcOH], gives a product containing some 24-chlorocoprostan-3-ol, since subsequent treatment with EtOH–NaOH affords some Δ^{24}-*norcoprosten*-3-*ol* (+0·5H_2O), m.p. 92—93°; (VII) is obtained from the non-cryst. material by successive treatment with Ac_2O, reduction, and hydrolysis. Et lithocholate and $MgPr^{\beta}Cl(Br)$ (6 mols.) give a little epi*coprostan*-3-*ol*-24-*one* (VIII), m.p. 177—178° [*Ac* derivative, m.p. 179—180°; *semicarbazone*, m.p. 241—242° (decomp.); *hydrazone*, m.p. 135—140° (decomp.)], and (mainly) 24-iso*propyl*epi*coprostane*-3 : 24-*diol* (+0·5H_2O) (IX), m.p. 106—107°, m.p. (anhyd.) 150—152° (*diacetate*, m.p .82—83°). (VIII) is oxidised (CrO_3, AcOH) to coprostane-3 : 24-dione, m.p. 184—186°, whilst (IX) (as acetate) gives (VIII). Wolff–Kishner reduction of (VIII) affords a *pinacol*, $C_{54}H_{94}O_4,H_2O$, m.p. 140—145°, m.p. (anhyd.) 182—183°, acetylated (Ac_2O) to a *diacetate*, m.p. 175—176° (X); an isomeric *diacetate*, m.p. 145—147° (XI), is obtained by reduction (H_2, PtO_2, AcOH) of the acetate of (VIII). (XI) is converted into (X) by boiling Ac_2O, whilst hydrolysis (EtOH–NaOH) of (X) and (XI) gives the pinacol. Clemmensen reduction of (VIII) affords a bimol. *compound*, $C_{54}H_{92(94)}O_3$, m.p. 196—197° (*diacetate*, m.p. 150—151°). MgMeI and (VIII) yield ψ-epi*ergostane*-3 : 24-*diol* (+0·5H_2O), m.p. 212—214°, m.p. (anhyd.) 223—224° also prepared from (VI) and $MgPr^{\beta}Br$, which with Ac_2O gives the *diacetate*, m.p. 165—166°, of ψ-epi*ergostanediol* 24 : 24′-*ether*, m.p. 208—209°. MgEtI and (VIII) yield ψ-epi*stigmastane*-3 : 24-*diol*, m.p. 240—241° [24 : 24′-*ether*, m.p. 186—188° (*diacetate*, m.p. 160—161°)]. Bisnor*epi*coprostane-3 : 23-diol (XII) (A., 1935, 1494) is converted by Ac_2O into the acetate (not characterised) of *bisnor*epi-Δ^{23}-*coprosten*-3-*ol* (+0·5H_2O), m.p. 120—123°, which is reduced (H_2, PtO_2, AcOH) to the *acetate*, m.p. 93—94°, of *bisnor*epi*coprostan*-3-*ol*, m.p. 134—135°. The latter is oxidised to bisnorcoprostanone [semicarbazone, m.p. 158—161° (decomp.)], which is reduced (H_2, PtO_2, AcOH–conc. HCl) to *bisnorcoprostan*-3-*ol* (XIII), m.p. 126—127° (*acetate*, m.p. 103—104°). Similar reduction of bisnorcoprostan-3-one-23-ol, m.p. 161—163° [semicarbazone, m.p. 173—175° (decomp.)], prepared by oxidation of (XII), gives a product (pptd. by digitonin) which on successive treatment with Ac_2O, reduction, and hydrolysis affords (XIII).

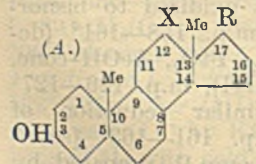
Comparison of the m.p. of various sterols and bile acids shows that the form pptd. by digitonin is more fusible than the *epi*-derivative in both the *cis*- and *trans*-series; shortening of the side-chain is generally accompanied by an increase in m.p. H. B.

Detection of oxycholesterol and its behaviour in the organism. K. Yamasaki (Fukuoka Acta med., 1935, 28, 109).—Oxycholesterol gives a blue colour with conc. H_2SO_4. Cholesterol exposed to solar radiation gives the blue colour and the m.p. is lowered. Nutr. Abs. (*m*)

Action of selenium dioxide on sterols and bile acids. II. Formation of isomeric dihydroxycholadienic acids from *apo*cholic acid and dihydroxycholenic acid; oxidation products of dihydroergosterol. R. K. Callow (J.C.S., 1936, 462—469).—Prep. of the dihydroxycholadienic acids

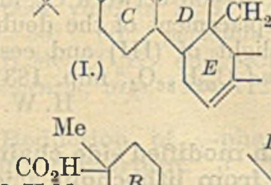
(I) obtained by action of Br on *apo*cholic acid (II) or on dihydroxycholenic acid (A., 1922, i, 1027; 1931, 957) or by other methods (A., 1931, 841; 1932, 615; 1933, 158) is repeated. Variation of [α] is due to (I) being varying mixtures of α-*dihydroxycholadienic acid* (III), m.p. 252—255°, $[\alpha]^{20}_{D}$ −35·3°, $[\alpha]^{20}_{5461}$ −47·7° (in EtOH), absorption max. at 243 mμ (broad) [obtained by action of BzO_2H on (II)], with β-*dihydroxycholadienic acid* (IV), m.p. 253—255°, $[\alpha]^{20}_{D}$ +71·0°, $[\alpha]^{20}_{5461}$ +82·1°, absorption max. at 249 mμ (sharp), with subsidiary max. at 242 mμ [obtained by action of aq. SeO_2 on (II) in EtOH]. Catalytic reduction of (III) yields (II); (IV) is reduced to β-apo*cholic acid*, m.p. 163—165°, $[\alpha]^{20}_{D}$ +78·5°, $[\alpha]^{20}_{5461}$ +92·4° [AcOH *compound* (V), m.p. 150—155°, $[\alpha]^{20}_{D}$ +73·5°, $[\alpha]^{20}_{5461}$ +86·5°; *xylene* compound, m.p. 156·5—161°; $[\alpha]^{20}_{D}$ +69·7°, $[\alpha]^{20}_{5461}$ +82·5°; *Me* ester (+1·5H_2O), m.p. 84—87°, $[\alpha]^{20}_{D}$ +79°, $[\alpha]^{20}_{5461}$ +90°, prepared from the *Ag* salt]. When (V) is treated with SeO_2, the resulting β-dihydroxycholadienic acid has m.p. 233—240°, $[\alpha]^{20}_{D}$ +77·7°, $[\alpha]^{20}_{5461}$ +92·8° (absorption max. at 250 mμ). When these are taken as the vals. for $[\alpha]^{20}_{D}$ and $[\alpha]^{20}_{5461}$ of (IV), and theoretical vals. of each for mixtures of (III) and (IV) are plotted against composition, observed $[\alpha]^{20}_{D}$ and $[\alpha]^{20}_{5461}$ for specimens of (I) from various sources indicate that these are a series of mixtures of (III) and (IV), the same composition being deduced for any one prep. from either $[\alpha]^{20}_{D}$ or $[\alpha]^{20}_{5461}$.

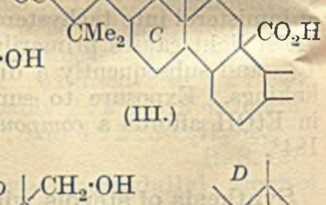
The $\Delta^{7:8}$-formula proposed by Wieland and Dane (A., 1932, 615; 1933, 158) for dihydroxycholenic acid (VI) is similar to that for γ-ergostenol, but since the latter is isomerised by Pt to non-reducible α-ergostenol, whilst (VI) is reduced normally, (VI) is now re-formulated as the $\Delta^{14:15}$-compound [*A*; X=OH, R=$C_4H_8{\cdot}CO_2H$ (cf. β-ergostenol)]. As (II) and (VI) are directly interconvertible, (II) is regarded as the $\Delta^{8:14}$ compound. Of the six conceivable positions of the ethylenic linkings in the dienic acids, absorption spectra and general chemical grounds eliminate all but the $\Delta^{7:8:14:15}$ $\Delta^{9:8:14:15}$ structures. As the latter would be expected to have the higher absorption at longer λ, (III) is regarded as the $\Delta^{7:8:14:15}$- and (IV) as the $\Delta^{9:8:14:15}$-compound. α- and β-*apo*Cholic acids differ in the position of H at $C_{(9)}$; SeO_2 attacks the latter position, BzO_2H the $C_{(7)}$. Ergosterol-*D* (A., 1933, 605) is regarded as the analogue of (IV), and thus formulated as the $\Delta^{9:8:14:15}$-compound (*A*; X=H, R=C_9H_{17}), ergosterol-B_3 as the analogue of (III), with the $\Delta^{7:8:14:15}$-structure, being derived from the decomp. of dihydroergosterol oxide, in which the oxide-bridge is in the 8 : 14-position.

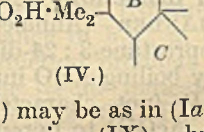

(*A*.)

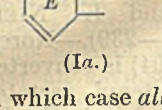
α-Ergostenol and SeO_2 give dehydroergostenol (3 : 5-*dinitrobenzoate*, m.p. 163—166°, $[\alpha]^{20}_{D}$ −3·0°, $[\alpha]^{20}_{5461}$ −5·7° in C_6H_6), which is now formulated as the $\Delta^{9:8:14:15}$-compound (*A*; X=H, R=C_9H_{19}). Me *apo*cholate and SeO_2 yield (IV), of which the *Ag* salt gives *Me* β-*dihydroxycholadienate*, m.p. 87—89°, $[\alpha]^{20}_{D}$ +62·5°, $[\alpha]^{20}_{5461}$ +71°. The oxidation of Me dihydroxycholenate (*bis*-3′ : 5′-*dinitrobenzoyl* derivative, m.p. 209—210·5°) and of β-*apo*cholic acid by SeO_2 and by BzO_2H is also studied. E. W. W.

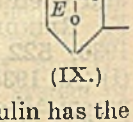
Polyterpenes and polyterpenoids. CVI. Oxidation of dihydrobetulin and dihydrobetulonic acid by nitric acid. L. Ruzicka and O. Isler (Helv. Chim. Acta, 1936, **19**, 506—509; cf. this vol., 607).—The prep. of betulin (I), dihydrobetulin (II), and dihydrobetulonic acid (III) is modified. (III) and fuming HNO_3 in AcOH at −5° to 0° give an *acid* (IV), $C_{27}H_{45}(CO_2H)_3$, m.p. 275° (*Me*$_3$ ester, m.p. 145°, liberates only 1 CO_2H with *N*-KOH–EtOH), which at 330°/high vac. gives CO_2 (1 mol.), H_2O (1 mol.), and a *keto-acid*, $C_{29}H_{46}O_3$, m.p. 259° [*oxime*, m.p. 278° (decomp.); *Me* ester, m.p. 178°, gives no colour with $C(NO_2)_4$]. (I) and HNO_3–AcOH give a *ketone* (V), $C_{30}H_{49}O_2{\cdot}NO_2$, m.p. 209°, an *acid* (VI), $NO_2{\cdot}C_{28}H_{47}O(CO_2H)_2$, m.p. between 158° and 170° according to the rate of heating [*Me*$_2$ ester, m.p. 124°; *anhydride* (VII), m.p. 215°; also obtained from (V) by CrO_3 or HNO_3]. (VI) and (VII) at 330° give CH_2O, also obtained from (V) at 260—300° along with a *substance*, ? $C_{29}H_{46}O$, m.p. about 200—204° (1 active H). The anhydride of the acid, $C_{30}H_{46}O_6$, from hydroxymethylene*allo*betulone has m.p. 193° (lit. 293°). These and previously recorded reactions lead to the formulæ shown, based on that (*loc. cit.*) for hederagenin (VIII). The ethylenic linking in (I) may be as in (I*a*), in which case *allo*betulin has the grouping (IX); but (I) is preferable, because the similar differences in [α] between the diols and diol acetates from (*a*) (I) and (II) and (*b*) hederabetulin and dihydrohederabetulin indicate a close relationship between (I) and (VIII).


(I.)


(III.)


(IV.)


(I*a*.)


(IX.)

[With M. Furter] *d* and *n* are determined for the diacetates of (I) and (II) above the m.p. R. S. C.

s-Di-*p*-anisylpinacol. C. W. Shoppee (J.C.S., 1936, 506—507).—Di-*p*-anisyl ketone (I) (2 : 4-*dinitrophenylhydrazone*, m.p. 197°) is reduced by Al–Hg in EtOH to 4 : 4′-dimethoxybenzhydrol (II) and *s*-di-*p*-anisylpinacol, new m.p. 183° (cf. A., 1933, 68) [decomp. to (I) and (II)]. The last with AcOH and a trace of I forms anisyl trianisylmethyl ketone (*loc. cit.*). Attempts to obtain the pinacol from Mg anisyl bromide and $Et_2C_2O_4$ (cf. Bouvet, Bull. Soc. chim., 1915, [iv], **17**, 209) gave an oil consisting mainly of $(p\text{-}OMe{\cdot}C_6H_4)_2C(OH){\cdot}CO_2Et$. Anisil and Mg *p*-anisyl bromide yield *anisoyldianisylcarbinol*, m.p. 117·5°. E. W. W.

Olivil. P. Dreyfuss (Gazzetta, 1936, **66**, 98—99).—Olivil Me$_2$ ether is oxidised by $K_2Cr_2O_7$–AcOH to the lactone of 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid (A., 1935, 860), to tetramethoxy-benzoylbenzoic acid and -phenylphthalide, and to a small amount of 2 : 3 : 6 : 7-tetramethoxyanthraquinone, apparently formed by way of an internal anhydro-compound. These results support the formulæ proposed (A., 1934, 1099) for olivil and for *iso*olivil. E. W. W.

Nitration of benzanilide and its derivatives. W. B. van Horssen (Rec. trav. chim., 1936, **55**, 245—262).—The action of abs. HNO_3 on several benzanilides (from the amine and acid chloride in tetralin) introduces NO_2-groups into both Ph radicals; the NO_2 enters the 3-position of the Bz unless one or more NO_2 are already present, when nitration is restricted to the NH_2Ph radical. The following are described: 3 : 5-*dinitrobenz-2′ : 4′-dinitro-*, m.p. 213°, 2-*nitrobenz-4′-nitro-*, m.p. 212°, 4-*nitrobenz-4′-nitro-*, m.p. 269°, 3 : 5-*dinitrobenz-4′-nitro-anilide*, m.p. 280°; 3-*nitrobenz-2′ : 6′-dinitro-*, m.p. 213°, 4-*nitrobenz-2′ : 6′-dinitro-*, m.p. 227°, 3 : 5-*dinitrobenz-2′ : 6′-dinitro*-p-*toluidide*, m.p. 275°; 3-*nitrobenz-*, m.p. 176°, 3-*nitrobenz-2′ : 6′-dinitro-*, m.p. 213°, 4-*nitrobenz-*, m.p. 231°. 4-*nitrobenz-2′ : 6′-dinitro-*, m.p. 210°, 3 : 5-*dinitrobenz-*, m.p. 237°, 3 : 5-*dinitrobenz-2′ : 6′-dinitro-4′-chloroanilide*, m.p. 265°; 3-*nitrobenz-*, m.p. 182°, 3-*nitrobenz-2′ : 6′-dinitro-*, m.p. 226°, 4-*nitrobenz-*, m.p. 247°, 4-*nitrobenz-2′ : 6′-dinitro-*, m.p. 214°, 3 : 5-*dinitrobenz*-p-*bromoanilide*, m.p. 251°. P. G. C.

Condensations by sodium. V. Preparation of acids. Dicarboxylic acids from monohalogen compounds. A. A. Morton, W. J. LeFèvre, and I. Hechenbleikner (J. Amer. Chem. Soc., 1936, **58**, 754—757; cf. A., 1932, 158).—PhCl, *m*- and *p*-C_6H_4MeCl, *p*-C_6H_4PhCl, and *o*-$C_6H_4Cl\cdot CHO$ with CO_2 (40—400 lb. pressure), and Na in C_6H_6 give BzOH (max. yield 78%), *m*- (88%) and *p*- (95%) -$C_6H_4Me\cdot CO_2H$, *p*-$C_6H_4Ph\cdot CO_2H$ (67%), and *o*-$CHO\cdot C_6H_4\cdot CO_2H$ (47%), respectively. With *n*-amyl chloride, CO_2, and Na in light petroleum, the following reactions occur: (i) Wurtz (predominates at pressures up to 100 lb.); (ii) $C_5H_{11}Cl+CO_2+2Na \rightarrow C_5H_{11}\cdot CO_2Na+NaCl$; (iii) $C_5H_{11}Cl+2CO_2+4Na \rightarrow 2NaCl+C_5H_{12}+CHBu(CO_2Na)_2$ (appreciable at 200—400 lb. pressure); (iv) formation of Na_2CO_3 and $Na_2C_2O_4$ (major products at higher pressures). The use of C_6H_6 as solvent leads to some *m*- and *p*-$C_6H_4(CO_2H)_2$. $AlkCO_2H$ and $CHAlk(CO_2H)_2$ or $CAlkAlk'(CO_2H)_2$ are formed (yields recorded) from EtCl, Bu^{a}Cl, *n*-hexyl and cetyl chlorides, β-chloropentane and -γ-methylbutane, and CH_2PhCl. H. B.

Differential reduction of the nitro-group by means of glucose. G. Bacharach and R. Weinstein (Rec. trav. chim., 1935, **54**, 931—933).—Reduction of *p*-$NO_2\cdot C_6H_4\cdot CO_2H$ with NaOH–H_2O–glucose at 50° gives *p-azoxybenzoic acid*, decomp. above 355°, and at 75° gives p-*azobenzoic acid*, decomp. above 300°. The concns. of the reagents in the two cases are specified. H. G. M.

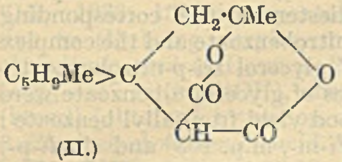
Iodo–silver nitrobenzoate complex and its action on some allyl derivatives. R. Jacquemain and A. Muskovits (Compt. rend., 1936, **202**, 497—499).—*o*-, *m*-, and *p*- (I) -$NO_2\cdot C_6H_4\cdot CO_2Ag$ when treated in dry C_6H_6 with I yield the corresponding *I-complexes* (cf. A., 1933, 711), which convert ethylene derivatives into the diester of the corresponding α-glycol. Thus allyl *p*-nitrobenzoate and the complex obtained from (I) yield glycerol tri-*p*-nitrobenzoate. The following derivatives of glycerol α-benzoate were similarly prepared in good yield from allyl benzoate: α′β-*di*-o-, m.p. 93°, α′β-*di*-m-, m.p. 103° and α′β-*di*-p-, m.p. 153°, -*nitrobenzoate*. H. G. M.

Two new dichloro-*o*-nitrobenzoic acids. P. Ruggli and H. Zaeslin (Helv. Chim. Acta, 1936, **19**, 434—439).—4 : 5-Dichloro-2-nitrotoluene and CrO_3–H_2SO_4 at $\not>$ −15° give 4 : 5-*dichloro-2-nitrobenzoic acid*, m.p. 165°, possibly identical with the acid, m.p. 160°, of Claus *et al.* (A., 1887, i, 828). 2 : 4 : 6-$C_6H_2Me(NO_2)_3$ and NH_4HS–EtOH give an 85% yield of 2-nitro-4 : 6-diaminotoluene, m.p. 135° (lit. 132°), converted, best (70%) by addition of aq. $NaNO_2$ to its solution with CuCl in conc. HCl at 50—70°, to 4 : 6-dichloro-2-nitrotoluene, m.p. 60° (obtained also much less well by other methods), oxidised with 15% HNO_3 at 150—160° (not by other methods) into 4 : 6-*dichloro-2-nitrobenzoic acid*, m.p. 189—190°. *p*-C_6H_4MeCl and fuming HNO_3 give a mixture of 2- and 3-NO_2- and 2 : 5-, 3 : 5-, and 2 : 6-$(NO_2)_2$-compounds (cf. lit.). 4-Chloro-2-nitrotoluene and fuming HNO_3 at 10—15° give 66% of 2 : 5- and 33% of 2 : 6-$(NO_2)_2$-compounds (cf. lit.). R. S. C.

Synthesis of 1 : 9-dimethyltetrahydrophenanthrene-2-carboxylic acid and of 1 : 9-dimethylphenanthrene. G. Darzens and A. Lévy (Compt. rend., 1936, **202**, 427—428; cf. A., 1935, 975).—1 : 4-$C_{10}H_6Me\cdot CH_2Cl$ gives *Et*$_2$ 4-*methyl-1-naphthylmethylmalonate*, b.p. 201—203°/2·5 mm., and thence *Et*$_2$ 4-*methyl-1-naphthylmethylallylmalonate* (α-4-*methyl-1-naphthyl-*Δ$^{\delta}$*-pentene-*ββ*-dicarboxylate*), hydrolysed to the corresponding *acid*, m.p. 184·5°, which decomposes at about 190° into α-4-*methyl-1-naphthylmethyl-*Δ$^{\gamma}$*-pentenoic acid*, m.p. 93·5°, and about 4% of the γ-*lactone*, b.p. 204°/2 mm. This acid is cyclised by H_2SO_4–AcOH (40°, 3 days) to 4 : 9-*dimethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene-2-carboxylic acid*, m.p. 201°; about 40% of the δ-*lactone*, m.p. 91°, is also formed. The acid with S at 230—300° yields 4 : 9-*dimethylphenanthrene-2-carboxylic acid*, m.p. 266°, but dehydrogenation with Se at 340—350° is accompanied by decarboxylation giving 1 : 9-dimethylphenanthrene [picrate, m.p. 163·5° (lit. 160°); *styphnate*, m.p. 181°]. All yields are good. H. G. M.

Keto–lactol tautomerism. V. Influence of methyl*cyclo*hexane rings on the tautomerism of δ-ketonic acids. M. Qudrat-i-Khuda and A. Mukherji (J.C.S., 1936, 570—573).—4-Methyl*cyclo*hexenylacetone (a mixture of Δ$^{\alpha}$- 30·3, and Δ$^{\beta}$- 69·7%, isomerides obtained from $CH_2Ac\cdot CO_2Et$–NaOEt–EtOH–4-methyl*cyclo*hexanone) heated with $CN\cdot CH_2\cdot CO\cdot NH_2$–NaOEt–EtOH gives 4-*methyl*-cyclo*hexane-1 : 4-spiro-2′-hydroxy-6′-keto-5′-cyano-2′-methylpiperidine* (I), m.p. > 300°, hydrolysed (conc. HCl) to the *dilactone* (II), m.p. 172°, converted by 10% NaOH and acidification at 0° into 1-*acetonyl*-

4-*methyl*cyclo*hexane*-1-*malonic acid* (*Ag* salt) which slowly reverts to (II), and is decarboxylated at 170° to the corresponding -1-*acetic acid* (III), b.p. 183°/6 mm. [*Ag* salt; *semicarbazone*, m.p. 195° (decomp.); *Me* ester, b.p. 120°/2 mm. (*semicarbazone*, m.p. 155°]. The anhydride of 4-methyl*cyclo*hexane-1 : 1-diacetic acid with boiling EtOH gives the *Et H* ester (*Ag* salt), converted by successive treatment with $SOCl_2$ and ZnMeI into *Et* 1-*acetonyl*-4-*methyl*cyclo*hexane*-1-*acetate*, b.p. 133°/3 mm. (*semicarbazone*, m.p. 140°), hydrolysed by KOH–aq. EtOH to (III). Reduction of (III) with Na–boiling EtOH affords the *lactone* (IV)



(II.)

$$C_5H_9Me{>}C{<}{\substack{CH_2{\cdot}CRMe\\CH_2\text{——}CO}}{>}O$$

(R=H), b.p. 142°/3 mm. By similar methods 3-methyl*cyclo*hexenylacetone affords the *imide*, m.p. > 300° [as (I)], hydrolysed to the *dilactone* [as (II)], m.p. 144°, hydrolysed to 1-*acetonyl*-3-*methyl*cyclo*hexane*-1-*malonic acid* (*Ag* salt), decarboxylated to the -1-*acetic acid* (V), b.p. 161°/2 mm. {*semicarbazone*, m.p. 212°; *Me* ester, b.p. 135—136°/13 mm. [*semicarbazone*, m.p. 162° (decomp.)]}. Similarly from 3-methyl*cyclo*hexane-1 : 1-diacetic anhydride are obtained the *Et H* ester (*Ag* salt), *Et* 1-*acetonyl*-3-*methyl*cyclo*hexane*-1-*acetate* (VI), b.p. 129°/5 mm. [*semicarbazone*, m.p. 105° (decomp.)], hydrolysed to (V), and converted by NaOEt into 3-methyl*cyclo*hexane*spirocyclo*hexane-3′ : 5′-dione. (VI) and MgMeI afford the *lactone* [as (IV), R=Me], b.p. 159°/10 mm. Reduction of (V) gives the *lactone* [as (IV), R=H], b.p. 187°/4 mm. The relative proportions of (III) and (II) formed in the 4- and 3-Me series are, respectively, 35·7 : 58 and 25 : 67%. J. W. B.

Derivatives of salicylic acid. IX. Stability of the sulphonic acid group in 4-sulphosalicylic acid. I. Nitration of 4-sulphosalicylic acid. X. II. Bromination of 4-sulphosalicylic acid. N. W. HIRWE and M. R. JAMBHEKAR (Proc. Indian Acad. Sci., 1936, **3**, A, 236—239, 261—264).—IX. 4-Sulphosalicylic acid (I) and HNO_3 (*d* 1·4)–Ac_2O at < 5° give a mixture of its 3 : 5-$(NO_2)_2$- (II), decomp. > 261° (K_2, *K H*, and *Ba*, $+2H_2O$, salts), and its 5-NO_2-derivative $+2H_2O$ (III), m.p. 166—167° (isolated as its *K H* salt by addition of conc. aq. KCl to the mother-liquor: *Ba* salt, $+H_2O$). When heated with HNO_3 (*d* 1·4) at 100° (I) gives 2 : 4 : 6-*trinitrophenol*-3-*sulphonic acid* $+4H_2O$, m.p. 105° (replacement of CO_2H by NO_2). Reduction of (III) with $(NH_4)_2S$–EtOH affords 5-*amino*-4-*sulphosalicylic acid*, decomp. > 260°. Similar reduction of (II) gives 3-*nitro*-5-*amino*-4-*sulphosalicylic acid*, decomp. > 280°, and with Fe–HCl the 3 : 5-$(NH_2)_2$-*acid*, decomp. > 290°, is obtained.

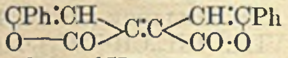
X. Passage of Br vapour into an aq. solution of (I) affords a mixture of its 5-*Br*-, $+4H_2O$, m.p. 210° (*Ba*, $+4H_2O$, and *K H* salts), 3 : 5-Br_2-, $+4H_2O$, m.p. 83° (*Ba*, $+H_2O$, and *K H* salts), and 3 : 5 : 6-Br_3-derivative, m.p. 115° (*Ba* salt). The non-replacement of CO_2H or SO_3H by Br results from the combination of the directing influences of OH and CO_2H, and of Br and SO_3H. J. W. B.

Condensation of chloral with salicylic acid. F. CALVET and M. N. MEJUTO (J.C.S., 1936, 554—556).—Condensation of $CCl_3{\cdot}CH(OH)_2$ and *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ in presence of conc. H_2SO_4 gives (after esterification) the *Me* ester (I), m.p. 200—202° (Ac_2 derivative, m.p. 207—209°), of βββ-*trichloro*-4 : 4′-*dihydroxy*-3 : 3′-*dicarboxy*-αα-*diphenylethane* (II), m.p. 290—292°, and 2-*hydroxy*-5-βββ-*trichloro*-α-*hydroxyethylbenzoic acid* (III), m.p. 180—182° [Ac_1 derivative, m.p. 190—192°, which gives a colour with $FeCl_3$; *Me* ester, m.p. 97—99° (Ac_1 derivative, m.p. 90—92°, giving no $FeCl_3$ colour)]. Condensation of (III)-*o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$–$H_2SO_4$ also gives (II). When boiled with KOH–MeOH (I) affords ββ-*dichloro*-4 : 4′-*dihydroxy*-3 : 3′-*dicarboxy*-αα-*diphenylethylene*, m.p. 295—297° (*Me* ester, m.p. 120—122°), and (III) similarly treated gives 6-hydroxy*iso*phthalaldehydic acid (IV), oxidised to 4-hydroxy*iso*phthalic acid which is also obtained by $KMnO_4$–NaOH oxidation of (III). Hydrolysis of (III) with conc. H_2SO_4 also gives (IV). Reduction of (III) with Zn–HCl–EtOH affords (?) 2-*hydroxy*-5-ββ-*dichlorovinylbenzoic acid*, m.p. 170—172°. J. W. B.

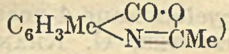
Isomeric, optically inactive menthyl mandelates. New type of racemism. A. MCKENZIE and E. M. LUIS (Ber., 1936, **69**, [*B*], 1118—1123).—Esterification of (+)-mandelic acid with (+)-menthol in presence of HCl at 100° yields (+)-*menthyl* (+)-*mandelate* (I), m.p. 81—82°, $[\alpha]^{18}_{D}$ +138·1°, $[\alpha]^{15}_{5461}$ +164·8° in EtOH. (+)-*Menthyl* r-*mandelate*, m.p. 85—86°, $[\alpha]^{15}_{D}$ +73·2° in EtOH, is obtained by direct esterification or mixing equal amounts of (I) and (+)-menthyl (−)-mandelate in $COMe_2$ and removing the solvent at room temp. dl-*Menthyl* (+)-*mandelate*, m.p. 76—77°, $[\alpha]^{16}_{D}$ +64·4° in EtOH, prepared by mixing equal amounts of (I) and (−)-menthyl (+)-mandelate in $COMe_2$ and removing the solvent, suffers partial resolution when recryst. successively from EtOH and light petroleum. dl-*Menthyl* r-*mandelate* (provisional nomenclature), m.p. 103—704°, is derived from equal amounts of (I) and (−)-menthyl (−)-mandelate, by esterification of *r*-mandelic acid by *dl*-menthol in presence of HCl, or from equal wts. of (+)- and (−)-menthyl *r*-mandelate. It is isomeric with *r*-menthyl *r*-mandelate, m.p. 80—81° (A., 1934, 777). The forms differ from one another in appearance. Each can be recryst. without change. The possibility of dimorphism appears excluded. Both isomerides can be isolated by fractional crystallisation from dil. alcohol of the product derived by mixing *dl*-menthyl (+)- with (−)-mandelate in equal proportions. Fractional esterification of *dl*-menthol with (−)-mandelic acid by Marckwald and McKenzie's method gives a lævorotatory unesterified alcohol. H. W.

Synthesis of 3-hydroxynaphthyl-2-acetic acid and of acylcarbinols. B. EISTERT (Ber., 1936, **69**, [*B*], 1074—1079; cf. A., 1935, 858).—Gradual addition of 3-acetoxy-2-naphthoyldiazomethane (I) to a suspension of Ag_2O in EtOH at 60° gives *Et* 3-*acetoxy*-2-*naphthylacetate* (II), b.p. 187—189°/4 mm., hydrolysed by 2*N*-NaOH to 3-*hydroxy*-2-*naphthylacetic acid*, m.p. 178—180° (decomp.), which passes when heated above its m.p. or, better, when boiled with Ac_2O, into 5 : 6-benzo-2-coumaranone (III). The "hydroxynaphthylacetic acid hydrate" (*loc. cit.*) is identified as the *K H* salt, $C_{12}H_{10}O_3,C_{12}H_9O_3K$, decomp. 243—244°. (II) and boiling NH_2Ph give 3-*hydroxynaphthyl*-2-*acetanilide*, m.p. 220—222°, converted by boiling Ac_2O into 3-*acetoxynaphthyl*-2-*acetanilide*, m.p. 196°, also obtained from (I), NH_2Ph, and Ag_2O in hot EtOH. (I) suspended in dioxan is transformed by 2*N*-H_2SO_4 at room temp. into 3-*acetoxy*-2-*naphthoylcarbinol*, m.p. about 120—124° (slight decomp.), transformed by boiling EtOH containing conc. HCl into (III), also obtained from (I) and 2*N*-H_2SO_4 in boiling EtOH. 1-Acetoxy-2-naphthoic acid, m.p. 158°, is converted by $SOCl_2$ in light petroleum at 80—90° into 1-*acetoxy*-2-*naphthoyl chloride*, m.p. 113—114° (gradual decomp.).

H. W.

Addition of aromatic hydrocarbons to maleic anhydride and green radicals from diaryldihydrofuranones. R. PUMMERER and E. BUCHTA (Ber., 1936, **69**, [*B*], 1005—1017).—It appears impossible to conduct the action between C_6H_6, maleic anhydride, and $AlCl_3$ so that phenylsuccinic anhydride and thence phenylmaleic anhydride are produced, the products being β-benzoyl- or, with PhMe, β-toluoyl- (I) -acrylic acid. If, however, hydrocarbon and $AlCl_3$ are used in large excess β-*toluoyl*-α-*tolylpropionic acid* (II), m.p. 151°, is obtained in 20% yield, also prepared from (I), PhMe, and $AlCl_3$. (II) is stable to $ClSO_3H$ at 15—20° but is converted by boiling AcCl containing a little conc. H_2SO_4 into the *dilactone* (III), $C_{36}H_{30}O_4$, decomp. 263° after softening and darkening, and by Ac_2O at 100° into (III) and the *monolactone* (IV), $C_{18}H_{16}O_2$, m.p. 104°. (IV) is transformed into (III) by Br in warm AcOH, by $FeCl_3$ in AcOH, or by warm Ac_2O containing a little H_2SO_4. (III) is converted into (IV) by reduction with Zn–Hg and boiling AcOH whereas Zn dust and AcOH convert it into a *substance*, $C_{36}H_{32}O_3$, m.p. 98°. (III) appears unchanged by hydrazobenzene in boiling PhCl. Oxidation of (III) by CrO_3 in AcOH affords *p*-$C_6H_4Me{\cdot}CO_2H$. (IV) is hydrolysed in the usual manner by KOH–MeOH whereas (III) is converted with difficulty into *di*-(β-*toluoyl*-α-*tolyl*)*propionic acid*, $C_{36}H_{34}O_6$, m.p. 166°. (III) and anhyd. $AlCl_3$ in PhCl at 120° yield a lactonic *acid*, $C_{36}H_{34}O_5$, m.p. 163°, reconverted into (III) when heated in Ac_2O at 100°. (II) and boiling N_2H_4,H_2O or (IV) and N_2H_4,H_2O in boiling EtOH afford 1 : 3-*ditolyl*-2 : 3 : 4 : 5-*tetrahydropyridazol*-4-*one*, m.p. 165°. 3 : 3′-*Di*-(5-N-*phenyl*-1 : 3-*ditolyl*-2 : 3 : 4 : 5-*tetrahydro*)*pyridazin*-4-*one*, m.p. 160°, is prepared from (III) and $NHPh{\cdot}NH_2$ in boiling xylene. When warmed in media of b.p. > 100° (III) dissociates into green radicals with marked red fluorescence. By analogy the constitution  is ascribed to Pechmann's dye. $CHBz{:}CH{\cdot}CO_2H$, $AlCl_3$, and PhMe at 100° give β-*benzoyl*-α-*tolylpropionic acid*, m.p. 149°. Fumaric acid is obtained from maleic anhydride, *m*-$C_6H_4(OH)_2$, and $AlCl_3$ in CS_2.

H. W.

Derivatives of benzoylbenzoic acids. M. HAYASHI, S. TURUOKA, I. MORIKAWA, and H. NAMIKAWA (Bull. Chem. Soc. Japan, 1936, **11**, 184—200).—3-Methylphthalic anhydride (I) (*imide*, m.p. 188·5—189°) condenses ($AlCl_3$) with C_6H_6 to give a *substance* (II), $C_{21}H_{16}O_2$, m.p. 116—117° (structures suggested), 2-*benzoyl*-3- (III), m.p. 171—172° (*Me* ester, m.p. 106·5—107·5°), and 2-*benzoyl*-6-*methylbenzoic acid*, m.p. 126·5—127·5° (*Me* ester, m.p. 122·5—123°) (also by the action of conc. H_2SO_4 on the -3-acid), oxidised by 1% $KMnO_4$ to *benzophenone*-2 : 6-, m.p. 255—256°, and -2 : 3-*dicarboxylic acid*, $+H_2O$, m.p. indefinite 121—146°, and anhyd., m.p. 140—141° (decomp.), respectively. (I) is converted by the usual methods into its 1-*Me* 2-*H*, $+H_2O$ and anhyd. (IV), m.p. 114·5—115°, *Me*$_2$ b.p. 169°/21 mm., and 1-*Et* 2-*H*, $+H_2O$, m.p. 75—85°, and anhyd., m.p. 86—87°, esters, and 4-methylphthalic anhydride (*imide*, m.p. 194·5—195°) into its 2-*Me* 1-*H*, $+H_2O$ and anhyd. (V), m.p. 89—90°, and *Et*$_2$ esters, b.p. about 193—195°/27 mm. The acid chloride of (IV) and C_6H_6–$AlCl_3$ give (II) and (III), and the acid chloride of (V) similarly affords 2-benzoyl-5-methylbenzoic acid (cf. below). (I) condenses with PhOH to give 2-(2′-*hydroxybenzoyl*)-, m.p. 220—221°, and 2-(4′-*hydroxybenzoyl*)-3-*methylbenzoic acid*, m.p. 197—198°, isomerised by conc. H_2SO_4 at room temp. to 2-(2′-*hydroxybenzoyl*)-, m.p. 141—142°, and 2-(4′-*hydroxybenzoyl*)-6-*methylbenzoic acid*, m.p. 183—184°, respectively. (I) and PhCl give (?) 2-(4′-*chlorobenzoyl*)-3-*methylbenzoic acid*, m.p. 175·5—176°. Contrary to Lawrance (A., 1920, i, 741) 3-nitrophthalic anhydride and C_6H_6 give only 3-*nitro*-2-*benzoylbenzoic acid* (VI), m.p. 236—237°. Condensation of the acid chloride of 1-Me 2-H 3-nitrophthalate with C_6H_6 gives only (VI), whereas the 2-Me 1-H ester gives mainly 6-*nitro*-2-*benzoylbenzoic acid*, m.p. 160—161°, and a little (VI). 2-Amino-6-, -3-, -5-, and -4-methylbenzoic acid and boiling Ac_2O afford, respectively, 6-, m.p. 84°, 3- (VII), m.p. 136—137°, 5- (VIII), m.p. 123—124°, and 4-*methylacetoanthranil*, m.p. 102—103° (all of type ). Acetoanthranil and C_6H_6 give 2-*anilino*-, m.p. 121·5—122° [*hydrochloride*, m.p. 165—167° (decomp.)], and 2-*amino-benzophenone*, m.p. 109—110° [*hydrochloride*, m.p. 179—180° (decomp.)]; (VII) similarly gives only 2-*anilino*-3-*methylbenzophenone*, m.p. 123—123·5° [*hydrochloride*, m.p. 166—173° (decomp.)], and (VIII) gives 2-amino- (IX) and 2-*anilino*-5-*methylbenzophenone*, m.p. 163·5°. Diazotisation of (IX), treatment with $Cu_2(CN)_2$ [*substance*, m.p. 189—190°, possibly di-(2-benzoyl-*p*-tolyl)amine, obtained], and hydrolysis of the crude nitrile affords 2-*benzoyl*-4-*methylbenzoic acid*, m.p. 150—150·5° [described in Part II (A., 1930, 1183) as the 5(or 4)-Me acid]; hence the 4(or 5)-Me acid, m.p. 145—145·5°, is 2-*benzoyl*-5-*methylbenzoic acid*. The following corrections to Parts III and IV (*loc. cit.*) are proposed: 2-(5′-chloro-2′-hydroxybenzoyl)-5-, m.p. 239·5—240·5° becomes -4-, and -4-, m.p. 227—228·5°, becomes -5-methylbenzoic acid. In all cases where the alternative 3(or 6)- and 6(or 3)-methylbenzoic acid occurs the first no. is correct.

J. W. B.

Synthesis of *cis*- and *trans*-*dl*-norcaryophyllenic acids and of dehydronorcaryophyllenic acid.

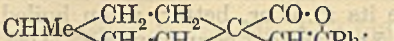
H. N. Rydon (J.C.S., 1936, 593—596).—ββ-Dimethyladipic acid (improved prep.) is converted by $SOCl_2$–Br into *Et αα′-dibromo-ββ-dimethyladipate*, b.p. 178—182°/12 mm., converted by NaCN–boiling EtOH and hydrolysis of the product with conc. HCl at 180° into *dl-trans*-3 : 3-dimethyl*cyclo*butane-1 : 2-dicarboxylic acid (I), m.p. 148—149°, identical with the *dl*-norcaryophyllenic acid (Ramage *et al.*, A., 1935, 489, 756, who describe it as *cis*) and converted by the method of these authors into 3 : 3-dimethyl-Δ^1-*cyclo*butene-1 : 2-dicarboxylic acid, m.p. 195°, identical with dehydronorcaryophyllenic acid. When heated with Ac_2O at 220° (I) affords (through the crude anhydride) the *dl-cis*-acid, m.p. 149—150°, converted by AcCl into the *cis*-anhydride, m.p. 40—41°, b.p. 100—102°/1 mm., identical with norcaryophyllenic anhydride (Ruzicka *et al.*, A., 1935, 351). The stereochemistry of norcaryophyllenic acid is still doubtful but (I) is certainly the *trans*-acid and the *dl*-acid, m.p. 149—150°, of Ruzicka *et al.* is the *dl-cis*-acid. The natural *d*-acid is probably *cis*. Neither α-*iso*propylglutaric acid (improved prep.) nor α-iso-*butylglutaric acid*, m.p. 68° [from $CHBu^{\beta}(CO_2Et)_2$–NaOEt–$CH_2Cl·CH_2·CO_2Et$ and hydrolysis], could be oxidised by CrO_3 to the α-OH-acid. γ-Carboxy-γ-*iso*heptolactone with PBr_5–PBr_3 affords *Et α-bromo-α-*iso*propylglutarate*, b.p. 138—142°/11 mm., and a *substance*, m.p. 126—127°, which contains Br.

J. W. B.

Valency-deflexion hypothesis. R. D. Desai (J. Univ. Bombay, 1935, 4, Part II, 206—214).—Mostly a brief review. 1-Carboxy-4-methyl*cyclo*hexane-1-acetic acid exists in only two forms (cf. A., 1931, 1055; 1935, 489). Attempts to isolate "extra" forms of six similar *cyclo*hexane derivatives failed. These and other data show failure of the usual methods to prove strain in the methyl*cyclo*hexane ring.

R. S. C.

Isomeric 1-carboxy-4-, -3-, and -2-methyl*cyclo*hexane-1-acetic acids. R. D. Desai, R. F. Hunter, G. Khan, and G. S. Saharia (J.C.S., 1936, 416—419).—Hydrolysis of *Et 1-cyano-4-methyl-*cyclo*hexane-1-α-cyanoacetate*, b.p. 162—164°/15 mm. (obtained by action of $CN·CHNa·CO_2Et$ on *1-hydroxy-1-cyano-4-methyl*cyclo*hexane*, b.p. 128°/20 mm., prepared from 4-methyl*cyclo*hexanone by $NaHSO_3$ and KCN), yields two 1-carboxy-4-methyl*cyclo*hexane-1-acetic acids, m.p. 137° (I) and 173° (II), identical with those obtained by oxidation of the two α-keto-4-methyl*cyclo*hexane-1 : 1-diacetic acids (A., 1932, 741). Repetition of the work of Qudrat-i-Khuda (A., 1931, 1055) shows that his *A* and *C* acids are identical with (I) and (II), but that his "*B*" is a mixture of *A* and *C* (cf. A., 1935, 489); "*D*" was not obtained. The anhydride (III), m.p. 104°, derived from (II) forms an *imide*, m.p. 171°, an *amic acid*, m.p. 195°, a p-*toluidinic acid*, m.p. 168—169°, a p-*tolylimide*, m.p. 160°, α- and β-*naphthylamic acids*, m.p. 140° and 185°, and α- and β-*naphthylimides*, m.p. 163° and 185°. The anhydride (IV), m.p. 77°, from (I) forms an imide, new m.p. 130°. In presence of $AlCl_3$, (III) and C_6H_6 yield *1-benzoyl-4-methyl*cyclo*hexane-1-acetic acid A* (V), m.p. 165° (*semicarbazone*, m.p. 165°), and a neutral *substance*, $C_{16}H_{18}O_2$, m.p. 160°, formulated as

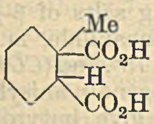


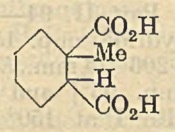
$$CHMe<\begin{matrix}CH_2·CH_2\\CH_2·CH_2\end{matrix}>C<\begin{matrix}CO·O\\CH:CPh\end{matrix}$$

(V) is reduced (Zn–Hg) to *1-benzyl-4-methyl*cyclo*hexane-1-acetic acid A*, m.p. 98°. (IV) and C_6H_6 yield *1-benzoyl-4-methyl*cyclo*hexane-1-acetic acid B* (VI), m.p. 140—141° (*semicarbazone*, m.p. 150°), with a neutral *substance*, m.p. 89°. Reduction of (VI) gives *1-benzyl-4-methyl*cyclo*hexane-1-acetic acid B*, m.p. 127°, with a neutral *substance*, $C_{16}H_{20}O_2$, m.p. 250°. *1-Hydroxy-1-cyano-3-methyl*cyclo*hexane*, b.p. 120°/15 mm., prepared from 3-methyl*cyclo*hexanone, yields ($CN·CHNa·CO_2Et$) *Et 1-cyano-3-methyl*cyclo*hexane-1-α-cyanoacetate*, b.p. 185°/15 mm., which is hydrolysed (HCl) to 1-carboxy-3-methyl*cyclo*hexane-1-acetic acid, m.p. 163° (decomp.) (VII), identical with that obtained by Desai (A., 1932, 741), and to a second form (VIII), m.p. 108° (*Ag* salt). The "third form" claimed by Desai and Hunter (A., 1935, 618) is a mixture of (VII) with (VIII). Treatment of Et 3-methyl*cyclo*hexylidenecyanoacetate with KCN followed by HCl yields (VII) and (VIII). (VII) forms an anilic acid, new m.p. 176° (decomp.), an anil, new m.p. 143°, an *imide*, m.p. 180—181°, a p-*toluidinic acid*, m.p. 180° (decomp.), p-*tolylimide*, m.p. 145°, α- and β-*naphthylamic acids*, m.p. 150° and 192° (decomp.), and α- and β-*naphthylimides*, m.p. 142° and 189°. (VIII) forms an *anhydride*, m.p. 50°, b.p. 145—148°/15 mm.; *anilic acid*, m.p. 207°; *anil*, m.p. 107°; *imide*, m.p. 92°; p-*toluidinic acid*, m.p. 185°; p-*tolylimide*, m.p. 102—103°; α- and β-*naphthylamic acids*, m.p. 207° and 183°; α- and β-*naphthylimides*, m.p. 115° and 116°. *1-Hydroxy-1-cyano-2-methyl*cyclo*hexane*, b.p. 114—116°/15 mm., prepared from 2-methyl*cyclo*hexanone (IX), yields *Et 1-cyano-2-methyl*cyclo*hexane-1-α-cyanoacetate*, b.p. 180°/15 mm., hydrolysed to two *1-carboxy-2-methyl*cyclo*hexane-1-acetic acids*, m.p. 170° (decomp.) [*anhydride*, b.p. 142—143°/12 mm.; *anilic acid*, m.p. 148°], and m.p. 160° [*anhydride*, b.p. 141—142°/12 mm.; *anilic acid*, m.p. 161—162°]. With $CN·CHNa·CO_2Et$, (IX) yields *Et 2-methyl*cyclo*hexylidenecyanoacetate*, b.p. 150—160°/15 mm., which with KCN yields the above pair of acids; since the m.p. of each of these differs from those of Qudrat-i-Khuda's "*B*" and "*D*" acids, Thorpe's suggestion (J.C.S., 1931, 1023) that the latter arose from (IX) in the starting material is eliminated. E. W. W.

Fused carbon rings. VIII. Dehydration of 2-methyl-1-Δ^{γ}-butenyl*cyclo*hexanol. D. C. Hibbit, R. P. Linstead, and A. F. Millidge. **IX. Synthesis of stereoisomeric 1-methyl*cyclo*hexane-1 : 2-dicarboxylic acids and of various methyl*cyclo*hexanecarboxylic-acetic acids. Influence of the angular methyl group on the stability of their anhydrides.** R. P. Linstead and A. F. Millidge (J.C.S., 1936, 476—478, 478—486).—VIII. $CH_2:CH·[CH_2]_2·MgBr$ and 2-methyl*cyclo*hexanone readily react in Et_2O to form *2-methyl-1-Δ^{γ}-butenyl*cyclo*hexanol*, b.p. 104—108°/18 mm. When heated with H_3PO_4, this is dehydrated to *2-methyl-1-Δ^{γ}-butenyl*cyclo*hexene*, b.p. 75—78°/10 mm., or, on prolonged heating, to *cis*-9-methyl-Δ^2-octahydronaphthalene (cf. this vol., 713), oxidised ($KMnO_4$) to two 1-methyl*cyclo*hexane-1 : 2-diacetic acids as before. The acid of m.p. 163—165° gives (MeOH–H_2SO_4) a *Me_2* ester, b.p. 122—125°/1 mm., and with $Ba(OH)_2$ yields 8-methyl-2-hydrindone.

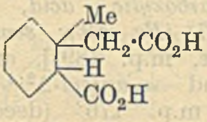
IX. The two forms of 1-methyl*cyclo*hexane-1 : 2-dicarboxylic acid are prepared. Et 1-methyl*cyclo*hexan-2-one-1-carboxylate, prepared by action of MeI on the Na derivative of Et *cyclo*hexan-2-one-1-carboxylate, is converted (HCN) into *Et 2-cyano-1-methyl*cyclo*hexan-2-ol-1-carboxylate*, b.p. 148—149°/12 mm., which on prolonged treatment with HCl gives 1-*methyl*cyclo*hexan-2-ol-1 : 2-dicarboxylic acid*, m.p. 166—167°. This with Ac_2O gives the *anhydride*, m.p. 86—87°, of 2-*acetoxy-1-methyl*cyclo*hexane-1 : 2-dicarboxylic acid*, m.p. 168°. The above cyanohydrin with $SOCl_2$ in C_5H_5N yields *Et 2-cyano-1-methyl-Δ^2-*cyclo*hexene-1-carboxylate*, b.p. 140—141°/9 mm. (not reduced by Al–Hg), hydrolysed to 1-*methyl-Δ^2-*cyclo*hexene-1 : 2-dicarboxylic acid*, m.p. 229—230° (decomp.) (*anhydride*, m.p. 67—68°; *Ag_2* salt; *Me_2* ester, b.p. 140°/11 mm.), which with 5% MeOH–H_2SO_4 gives 2-*carbomethoxy-1-methyl-Δ^2-*cyclo*hexene-1-carboxylic acid*, m.p. 112—114°. When the Me_2 ester is heated with KOH–MeOH, 1-*carbomethoxy-1-methyl-Δ^2-*cyclo*hexene-2-carboxylic acid*, m.p. 119—120°, is formed. The Me_2 ester is hydrogenated (Adams) to a mixture of saturated *esters*, b.p. 122—129°/9 mm. [hydrolysed to a mixed *acid* (I), m.p. about 170°], which is treated with K in Et_2O, followed by dil. acid; hydrolysis of the resulting *ester*, b.p. 124—126°/10 mm., with HCl gives a mixture, m.p. 200°, containing 40% of *cis*-acid, recrystallised to give β- or trans-1-*methyl*cyclo*hexane-1 : 2-dicarboxylic acid* (II), m.p. 213°. The mixture (I) treated with conc. HCl at 190° gives 85% of *cis*-acid, recrystallised to α- or cis-1-*methyl*cyclo*hexane-1 : 2-dicarboxylic acid* (III), m.p. 160°. The composition of mixtures of (II) and

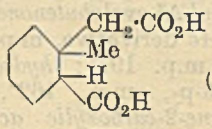
(III.) 

 (II.)

(III) is determined by thermal analysis. (II) forms (AcCl) the trans-*anhydride*, m.p. 80°. (III) with Ac_2O gives an *anhydride*, m.p. 60—65°, b.p. 144—146°/19 mm., hydrated to an 80% *cis*-acid. (II) and (III) are both racemates; their constitutions are based on analogy and are not certain. (III) and (II) are considered to be *cis* and *trans* since their anhydrides are low- and high-melting, respectively, resembling those of *cis*- and *trans*-hexahydrophthalic acid; also the anhydride of (III) is the more stable; this evidence is preferred to that of the action of HCl on (I). The action of angular Me is to stabilise the *cis*-form.

Both forms of 1-methyl*cyclo*hexane-1-carboxylic-2-acetic acid have been synthesised from Et 2-methyl*cyclo*hexanone-2-carboxylate, which with $CN\cdot CH_2\cdot CO_2Et$ and $C_5H_{11}N$ at room temp. gives no condensation products, but at very high pressure forms *Et_2 2-methyl*cyclo*hexylidene-1-cyanoacetate-2-carboxylate* (IV), b.p. 160—165°/1 mm., which deposits a small amount of solid, m.p. 85—86°. (IV) reduced (Al–Hg) and hydrolysed yields cis-1-*methyl*cyclo*hexane-1-carboxylic-2-acetic acid*, m.p. 174—175°. The *cis*-configuration is assigned by analogy with previous results; (V) differs from the isomeride obtained by Chuang *et al.* (A., 1935, 859), which is therefore the *trans*-form, identical with that obtained from 8-methyl-2-hydrindanone (this vol., 713). Attempted prep. of (V) from 1-*methyl*cyclo*hexanol-2-acetic acid lactone*, b.p. 140—141°/15 mm. (obtained from Et *cyclo*hexanone-2-acetate and MgMeI), is unsuccessful. Both forms of 1-methyl*cyclo*hexane-2-carboxylic-1-acetic acid are prepared. 1-Carbethoxy-9-methyldecahydronaphthalene-2 : 4-dione is hydrolysed to 9-methyldecahydronaphthalene-2 : 4-dione, which with NaOBr gives a mixture of *cis*- (VI), m.p. 171·5°, and *trans*-1-methyl*cyclo*hexane-2-carboxylic-1-acetic acid (VII), m.p. 131—132°. Mixtures are determined by thermal analysis. (VII) with Ac_2O gives the trans-

(VI.) 

 (VII.)

anhydride, b.p. 163—165°/19 mm.; (VI) an *anhydride*, m.p. 50°, b.p. 152—154°/19 mm., hydrolysed to 45% of *cis*-acid, from which (VII) is isolated. (VII) is almost unchanged by HCl at 190—200°, but (VI) gives 90% of (VII). (VI) with 20% $Ba(OH)_2$ at 350° gives the *cis*-anhydride (no ketone). Arguments for the *cis*- and *trans*-structures of (VI) and (VII) are discussed. (VI) is synthesised from the lower homologue. With H_2 and Ni at 220—240°, the anhydride of (III) gives only a hydrocarbon, b.p. 130—140° (1 : 2-dimethyl*cyclo*hexane?), but with EtOH and Na, it yields a *lactone*, b.p. 129—132°/12 mm., which is probably a mixture of 2-*methylol-1-methyl*cyclo*hexanecarboxylic acid lactone* with the 2-*Me* isomeride, and with KCN at 280—290° yields a *CN*-acid hydrolysed to (VI).

Two forms of 1-methyl*cyclo*hexane-2-carboxylic-3-acetic acid are synthesised. The *cyanohydrin* of 2-methyl*cyclo*hexanone is obtained as a semi-solid mixture of stereoisomerides, b.p. 122—123°/10 mm., dehydrated by $SOCl_2$ and C_5H_5N to *tetrahydro-*o*-toluonitrile*, b.p. 85—86°/10 mm. This is probably a mixture of the Δ^1- and Δ^6-forms, but only the latter reacts with Na, EtOH, and $CH_2(CO_2Et)_2$, forming *Et_2 2-cyano-1-methyl*cyclo*hexane-3-malonate*, b.p. 180—188°/11 mm., hydrolysed to a mixture of "cis"-, m.p. 164—165°, and "trans"-1-*methyl*cyclo*hexane-2-carboxylic-3-acetic acid*, m.p. 138—140° (*Ba* salts). With HCl at 200°, the former gives the latter. α-Methylglutaconic acid (improved prep.) forms a *Me_2* ester, b.p. 117°/13 mm. Attempted condensation of butadiene with this or with *Me_2 β-methylglutaconate*, b.p. 109—110°/12 mm., to give methyl*cyclo*hexane-carboxylic-acetic acids was unsuccessful. E. W. W.

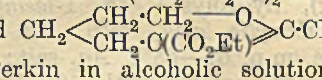
Condensation of phenols and phenolic ethers with acetonedicarboxylic acid. II. β-Substituted *cyclo*butenonecarboxylic acids. V. M. Dixit (J. Univ. Bombay, 1935, 4, Part II, 153—160; cf. A., 1932, 512).—The keto-acids obtained (*loc. cit.*) from $CO(CH_2\cdot CO_2H)_2$ and PhOH, *o*- and *p*-$C_6H_4Me\cdot OMe$ are 3-*aryl-Δ^2-*cyclo*butenone-2-carboxylic acids*, because of the following reactions. The 3-*p*-hydroxyphenyl-acid, m.p. 224°, more readily obtained by a modified method, is monobasic (*Ba* salt), is obtained from β-*p*-hydroxyphenylglutaconic acid (I) by heating alone at 195° or with AcCl at 100°, and is converted into (I) by 10% NaOH; it gives *Ac_2* (II), m.p. 123° (*Ba* salt), and *Ac* derivative (III), m.p. 171°; with PCl_3 at 100° it affords 1-*chloro*-3-p-*hydroxyphenyl*-$\Delta^{2:4}$-cyclo*butadiene*-2-*carboxylic acid* (IV), m.p. 143°; it gives a *semicarbazone*, m.p. 258° (decomp.), *hydrazone*, m.p. 193°, and *oximino*-derivative, m.p. 201° (decomp.). (III) gives a *semicarbazone*, m.p. 279°, and *oximino*-derivative, m.p. 212°, with Ac_2O yields (II), with PCl_3 the *Ac* derivative, m.p. 126°, of (IV), and with dil. NaOH the Ac derivative of (I). *p*- and *o*-Cresol afford similarly 3-p-, m.p. 160° (*Ac* derivative, m.p. 118°; *semicarbazone*, m.p. 213°; *hydrazone*, m.p. 188°), and -o-*anisyl*-Δ^2-cyclo*butenone-2-carboxylic acid*, m.p. 166° [*Ac* derivative, m.p. 137° (*Ba* salt); *semicarbazone*, m.p. 197°; *hydrazone*, m.p. 189°], and 1-*chloro*-3-p-, m.p. 162°, and -o-*anisyl*-$\Delta^{2:4}$-cyclo*butadiene-2-carboxylic acid*, m.p. 176° (decomp.). The "anhydride" obtained (J.C.S., 1912, **107**, 859) from β-phenylglutaconic acid and AcCl is considered to be a similar cyclic compound. R. S. C.

Dehydrogenation. III. Dehydrogenation of hydroaromatic carboxylic acid derivatives and ketones by selenium. L. Ruzicka (Helv. Chim. Acta, 1936, **19**, 419—423; cf. A., 1935, 738).—Hydroaromatic substances containing groups derived from CO_2H may give with Se aromatic acids or methylated hydrocarbons. Hydroaromatic ketones may give phenols. Et Δ^1-tetrahydro-*o*-toluate with Se at 360° gives PhMe and *o*-$C_6H_4Me\cdot CO_2H$. Me_2 1 : 3 : 3-trimethyl-Δ^1-*cyclo*hexene-4 : 5-dicarboxylate at 360° gives *m*-xylene-4 : 5-dicarboxylic anhydride, m.p. 115—116°, sublimes at 100°/0·1 mm. [corresponding acid, m.p. 183° (loss of H_2O)], also obtained, but only at 400°, from Me_2 1 : 3 : 3-trimethyl*cyclo*hexane-4 : 5-dicarboxylate. 1 : 1-Dimethyloctahydronaphthalene-6 : 7-dicarboxylic anhydride [from myrcene (I) and maleic anhydride] at 330—350° gives 1 : 6 : 7-$C_{10}H_5Me_3$, which proves conclusively the position of the ethylenic linkings in (I). *trans*-β-Decalone at 260° gives β-$C_{10}H_7\cdot OH$ and a *substance*, $C_{20}H_{12}Se$, m.p. 307—308°, whilst 3-methyl-Δ^2-*cyclo*hexenone gives *m*-cresol. R. S. C.

Oxidation of *iso*safrole. M. Imoto (J. Soc. Chem. Ind. Japan, 1936, **39**, 132B; cf. A., 1934, 403).—The yield of piperonylic acid obtained from *iso*safrole and the theoretical amount of $KMnO_4$ is increased by various catalysts, most (to 62·8%) by active C. R. S. C.

Synthesis of α-substituted glutaconic acids. N. L. Phalnikar and K. S. Nargund (J. Univ. Bombay, 1935, **4**, Part II, 106—108).—Esters, $CH_2R\cdot CO_2Et$ (R = Me, CH_2Ph, or Ph), with HCO_2Et and "mol." Na give the α-aldehydo-acids, which are condensed without isolation with $CH_2(CO_2H)_2$ and piperidine to give Et H glutaconates; purification by way of the Et_2 esters and subsequent hydrolysis then affords *trans*-α-methyl-, m.p. 144° (Et_2 ester, b.p. 180—185°/120 mm.), -benzyl-, and -*phenyl-glutaconic acid*, m.p. 164° (*Et_2* ester, b.p. 220°/80 mm.). R. S. C.

Condensation of phenylpyruvic acid with acetophenone. P. Cordier (Compt. rend., 1936, **202**, 1440—1442).—Interaction of $CH_2Ph\cdot CO\cdot CO_2H$ with COPhMe in aq. KOH–EtOH affords, after treatment with dil. HCl, α-*hydroxy*-β-*benzoyl*-α-*benzylpropionic acid*, m.p. 140°, which is unchanged by cold HCl, but with hot HCl in AcOH is converted into β-*benzoyl*-α-*benzylidenepropionic acid* (I), m.p. 160—165° (decomp.), and 2-*keto*-5-*phenyl*-3-*benzylidene*-2 : 3-*dihydrofuran*, m.p. 149—150°, easily hydrolysed to (I). J. L. D.

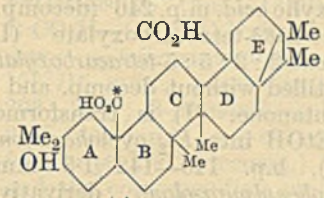
Syntheses in the thujane group. I. Synthesis of ketopolymethylene-1 : 3-dicarboxylic esters. P. C. Guha and N. K. Seshadriengar (Ber., 1936, **69**, [*B*], 1207—1212).—$CH_2(CH_2Br)_2$ and the Na derivative of $CO(CH_2\cdot CO_2Et)_2$ in C_6H_6 give the compound  $CH_2{<}\begin{matrix}CH_2\cdot CH_2—O\\CH_2\cdot C(CO_2Et)\end{matrix}{\geqslant}C\cdot CH_2\cdot CO_2Et$ (obtained by Perkin in alcoholic solution) and compounds obtained by the action of Na on $CO(CH_2\cdot CO_2Et)_2$. $CH_2(CH_2Br)_2$ and the Mg derivative of $CO(CH_2\cdot CO_2Et)_2$ in boiling EtOH afford *Et_2* cyclo*hexanone*-1 : 3-*dicarboxylate*, b.p. 142°/2 mm., hydrolysed by boiling H_2SO_4 (1 : 1) to *cyclo*hexanone, unchanged material, $CH_2Ac\cdot CO_2Et$, and Et *cyclo*hexanonecarboxylate. Under similar conditions $C_2H_4Br_2$ gives *Et_2* cyclo*pentanone*-2 : 5-*dicarboxylate*, b.p. 143°/4 mm. (*Cu* derivative, m.p. 200°), hydrolysed to *cyclo*pentanone, whilst CH_2Br_2 affords Et_2 *cyclo*butanone-2 : 4-dicarboxylate and two *compounds*, m.p. 102° and 286°, respectively. H. W.

Degradation of β-anisyl- and β-halogenoanisylglutaric acids to succinic acids through γ-butyrolactones and other reactions [thereof]. D. B. Limaye and R. G. Chitre (J. Univ. Bombay, 1935, **4**, Part II, 94—103).—Ag salts of β-*p*-anisyl- (I) [anhydride, m.p. 152°; monoanilide, m.p. 157°; Et_2, b.p. 206°/14 mm., *Et H*, m.p. 78°, and (*$COPh\cdot CH_2$*)$_2$ ester, m.p. 95°] and β-3-halogeno-*p*-anisyl-glutaric acids with I at 150° do not give butyrolactones. Ag β-3 : 5-dihalogeno-*p*-anisylglutarates, however, give CO_2 and butyrolactones, which with $K_2Cr_2O_7$ give the substituted succinic acids. (I) is substituted, yielding the 3-*I*-derivative, m.p. 160° [*anhydride*, m.p. 148°; *monoanilide*, m.p. 182°; *Et_2*, m.p. 83°, *Me_2*, m.p. 79°, and (*$COPh\cdot CH_2$*)$_2$ ester, m.p. 131°], also obtained by I and HIO_3 in hot H_2O. The substituted Et_2 glutarates with $Et_2C_2O_4$ and "mol." Na (not NaOEt) give *cyclo*pentadione derivatives. The following are described; direct halogenation, where recorded, is effected in AcOH. β-3-*Bromo*- [from (I)], m.p. 147° [*anhydride*, m.p. 143°; *monoanilide*, m.p. 150°; *Et_2*, m.p. 66°, *Me_2*, m.p. 74°, and (*$COPh\cdot CH_2$*)$_2$ ester, m.p. 125°], -3-*chloro*- [from (I)], m.p. 157° (*anhydride*, m.p. 128°; *monoanilide*, m.p. 143°; *Et_2*, m.p. 40·5°, and *Me_2* ester, m.p. 59°), -3 : 5-*dichloro*- [from (I)], m.p. 195° [*anhydride*, m.p. 182°; *monoanilide*, m.p. 172°; *Et_2*, b.p. 320° (decomp.), *Me_2*, m.p. 63·5°, and (*$COPh\cdot CH_2$*)$_2$ ester, m.p. 120°], and -3 : 5-*dibromo*-p-*anisylglutaric acid*, m.p. 211° [*anhydride*, m.p. 233°; *monoanilide*, m.p. 180°; *Et_2*, b.p. 315° (decomp.), and *Me_2* ester, m.p. 62°]. β-3 : 5-*Di-chloro*-, m.p. 72°, and -*bromo*-p-*anisyl-γ-butyrolactone*, m.p. 98°. 3 : 5-*Di-chloro*- [also obtained from $CO_2H{\cdot}CH_2{\cdot}CH(C_6H_4{\cdot}OMe){\cdot}CO_2H$ (II) and Cl_2–AcOH), m.p. 173°, and *-bromo-* [also obtained from (II) and dry Br at 100°], m.p. 198° (*anhydride*, m.p. 110°), and 3-*bromo*-p-*anisylsuccinic acid*, m.p. 175° (*anhydride*, m.p. 168°). *Et*$_2$ 1-p-*anisyl-*, m.p. 123°, 1-3′-*chloro-*, m.p. 126°, *-bromo-*, m.p. 129°, *-iodo-*, m.p. 133°, -3′ : 5′-*dichloro-*, m.p. 164°, and *-dibromo*-p-*anisyl*-cyclo*pentadione*-2 : 5-*dicarboxylate*, m.p. 168°. 3 : 5-Dibromo-*p*-anisaldehyde [*semicarbazone*, m.p. 236° (decomp.); *phenylhydrazone*, m.p. 135°] could not be condensed with $CN{\cdot}CH_2{\cdot}CO_2Na$. 3 : 5-*Dibromo-4-hydroxybenzaldehydesemicarbazone* has m.p. 233° (decomp.). R. S. C.

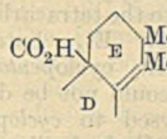
Methoxylated *o*-benzoylbenzoic acids. C. Weizmann and E. Bergmann (J.C.S., 1936, 567—569).—Demethylation by $AlCl_3$ in condensations occurs only if the reaction is slow. Thus phthalic anhydride (I) with α- and β-$C_{10}H_7{\cdot}OMe$, and 1 : 5-$C_{10}H_6(OMe)_2$ and $AlCl_3$ at room temp. afford, respectively, *o*-4′- and *o*-2′-methoxy- [also from (I) and the Mg compound of 1 : 2-$C_{10}H_6Br{\cdot}OMe$] and *o*-1′ : 5′-dimethoxy-4′-naphthoylbenzoic acid. Pyrogallol Me_3 ether and 2 : 3-$C_{10}H_6(CO)_2O$ or hemipinic anhydride (II) with $AlCl_3$ in CS_2 give, respectively 3-(4′-hydroxy-2′ : 3′-dimethoxybenzoyl)-2-naphthoic acid and 6-(4′-hydroxy-2′ : 3′-dimethoxybenzoyl)-2 : 3-dimethoxybenzoic acid. *o*-(2′ : 3′ : 4′-Trimethoxybenzoyl)benzoic acid, m.p. 196°, is obtained by the action of (I) on 4-lithio-1 : 2 : 3-trimethoxybenzene (N_2), the product, m.p. 169° (Bentley *et al.*, J.C.S., 1908, **93**, 436) being partly demethylated. (II) and MgPhBr afford 2-benzoyl-3 : 4-dimethoxybenzoic acid, cyclised by H_2SO_4 to alizarin 1 : 2-Me_2 ether and a *substance*, m.p. 192°. (II) and α-$C_{10}H_7{\cdot}MgBr$ give 2-α-naphthoyl-3 : 4-dimethoxybenzoic acid, cyclised to 1 : 2-dimethoxy-7 : 8-benzanthraquinone; (II) and the Mg compound of 2 : 6-$C_{10}H_6Br{\cdot}OMe$ give 2-(6′-methoxy-β-naphthoyl)-3 : 4-dimethoxybenzoic acid, dimorphous, m.p. 237° and 240°. J. W. B.

Dyes derived from acetylenedicarboxylic acid. R. N. Misra and S. Dutt (J. Indian Chem. Soc., 1936, **13**, 98—103).—$(⁝C{\cdot}CO_2H)_2$ (I) condenses with some phenols and amines, preferably in presence of $SnCl_4$ or a little conc. H_2SO_4, to yield dyes which are more deeply coloured (generally pink in alkali) and possess higher absorption max. than analogous compounds containing C⁝C (cf. A., 1927, 969). The following are described: *phenol-* (II), m.p. 119—120° (decomp.) (softens at 115°), *resorcinol-*, decomp. 185° [*Br*$_4$-derivative, m.p. 115—117° (decomp.)], *phloroglucinol-*, m.p. >310°, *orcinol-*, m.p. 155—157° (decomp.), m-*dimethyl-*, m.p. 126° (decomp.), and m-*diethyl-*, m.p. 109° (decomp.), *-aminophenol-*, and m-*phenylenediamine-*, decomp. 260°, *-acetylenein*. Solutions of these [except (II)] show strong fluorescence. Condensation does not occur with *o*- and *p*-cresol, *m*-$NH_2{\cdot}C_6H_4{\cdot}OH$, and *o*-, *m*-, and *p*-xylenols; pure products could not be isolated from (I) and *o*-$C_6H_4(OH)_2$ or pyrogallol. H. B.

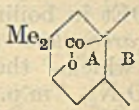
Quinovic acid. V. H. Wieland, A. Hartmann, and H. Dietrich (Annalen, 1936, **522**, 191—217).—Dehydrogenation (Se at 350—360°; Pd–C at 340—350°) of quinovic (I) or pyroquinovic (II) acid gives a *hydrocarbon* (III), $C_{24}H_{24}$ or $C_{26}H_{26}$, m.p 202—203°, together with the trimethylpicene (IV), m.p. 306° (corr.) [previously described (A., 1932, 945) as a hydrocarbon $C_{20}H_{16}$], obtained by Ruzicka *et al.* (cf. A., 1934, 530) from various sapogenins. Siaresinolic acid is also dehydrogenated (Se at 310—320°) to a little (IV); the main products are [unlike (I) or (II)] $C_{10}H_8$ derivatives. (IV) is oxidised (CrO_3, AcOH) to an o-*quinone*, $C_{25}H_{18}O_2$ (?), m.p. 252—255° (decomp.), purified by adsorption on activated Al_2O_3; (III) similarly gives non-cryst. material. Structure (*A*) is now assigned to (I); (II) is formulated as (*B*) with $\overset{*}{C}O_2H{=}H$.



(*A*.)

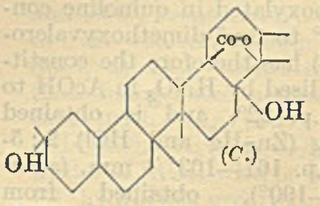


(*B*.)



(V.)

Oxidation (2% $KMnO_4$, 0·5% KOH, 60°) of novic acid (V) gives a *hydroxyketo-acid* (VI), $C_{30}H_{42}O_6$, m.p. 237—238° (*Me*$_1$ ester, m.p. 198°), and a little of an *isomeride*, m.p. 262° [also formed in small yield by oxidation of (V) with CrO_3 in AcOH]. (VI) is oxidised (CrO_3, AcOH) to novicquinone (A., 1930, 600) (structure suggested), which is further oxidised (30% H_2O_2, AcOH) to a dilactonic *dicarboxylic acid*, $C_{30}H_{42}O_8$, m.p. 287—288° (decomp.) (*Me*$_2$ ester, m.p. 242°). Thermal decomp. of (VI) at 260° affords a 3 : 2 mixture of two isomeric neutral *substances*, $C_{29}H_{40}O_3$, m.p. 218° and 242—243°. Oxidation (CrO_3, AcOH) of diacetylpyroquinovic acid is now considered (cf. *loc. cit.*) to give the Ac_1 derivative, m.p. 289° (*Me* ester, m.p. 220°), of a OH-acid, $C_{29}H_{42}O_5$; the latter is then similarly oxidised to a *CO-acid* (VII), $C_{29}H_{40}O_5$, m.p. 290° (decomp.) [*Me*$_1$ ester, m.p. 219°; *Br*-derivative, m.p. 192—194° (decomp.)]. (II), which gives a violet colour with Ac_2O–conc. H_2SO_4, is similarly oxidised at 20° or 60° to (VII), an *acid*, $C_{29}H_{42}O_6$, m.p. 318° (decomp.) (*Me*$_1$ ester, m.p. 195°), and (VIII) (below); oxidation at 100° affords a non-cryst. product which when distilled in a high vac. yields a neutral *substance*, $C_{29}H_{36}O_5$, m.p. 273—274°. (II) absorbs 1 O when treated with BzO_2H in $CHCl_3$, but the *dihydroxylactone* (*C*), m.p. 267° (decomp.) [*Ac*$_1$ derivative, m.p. 298—300° (decomp.)], is produced; this is identical with the compound previously obtained (A., 1931, 1158) by ozonolysis of (II) and it is oxidised (CrO_3, AcOH) to the *hydroxyketolactone* (VIII), m.p. 286—288° (cf. *loc. cit.*).



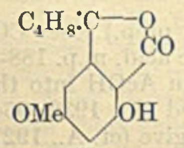
(*C*.)

Anhydroquinovic acid (simplified prep.) loses CO_2 at 245° to give pyroanhydroquinovic acid, m.p. 188—189°, which is converted by $ZnCl_2$ in AcOH into the same lactone as is similarly obtained (A., 1932, 954) from (II). (I) and cold conc. H_2SO_4 give (cf. A., 1927, 562) quinochromin (IX), m.p. 249°, and iso*quinochromin*, $C_{29}H_{42}O_2$, m.p. 205—206°. (IX) is unsaturated (catalytic reduction; Br in AcOH–NaOAc;

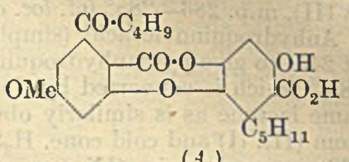
cryst. products not isolable) and is reduced (Na, EtOH) to a *dihydro*-derivative, m.p. 177—178°. H. B.

Syntheses in the thujane group. II. Synthesis of northujone-2 : 6-dicarboxylic esters. P. C. Guha and N. K. Seshadriengar (Ber., 1936, 69, [*B*], 1212—1218).—Addition of $COBr_2$ in Et_2O to the Na derivative of Et_4 pentane-ααεε-tetracarboxylate (I) [prep. from $CH_2(CO_2Et)_2$ and $CH_2(CH_2Br)_2$ described] yields *Et_4* cyclo*hexanone-*2 : 2 : 6 : 6*-tetracarboxylate*, b.p. 177°/1 mm. (corresponding *tetra-anilide*, m.p. 305°), hydrolysed and decarboxylated by H_2SO_4 to *cyclo*hexanone and by cold, 10% KOH–EtOH to the tetracarboxylic *acid*, m.p. 246° (decomp.). Similarly Et_4 butane-ααδδ-tetracarboxylate (II) yields Et_4 cyclo*pentanone*-2 : 2 : 5 : 5-*tetracarboxylate*, which could not be distilled without decomp. and is hydrolysed to *cyclo*pentanone. (I) is transformed by NaOEt in boiling EtOH into *Et_2* cyclo*hexanone*-2 : 6-*dicarboxylate* (III), b.p. 140—142°/1·3 mm., from which the *phenylpyrazolone* derivative, $C_{16}H_{18}O_3N_2$, m.p. 150°, *pyrazolone* derivative, $C_{10}H_{14}O_3N_2$, m.p. 156—157°, the corresponding *dianilide*, m.p. 259—260°, and the *amide*, m.p. 225°, are obtained. The successive action of Na and Br on (III) in Et_2O leads to *Et_2* dicyclo-[0 : 1 : 3]-*hexan-*1-*one*-2 : 6-*dicarboxylate*, which could not be distilled without decomp.; its structure is established by its oxidation to *cyclo*pentane-1 : 2-dicarboxylic acid. (II) and NaOEt in boiling EtOH afford *Et_2* cyclo*pentanone*-2 : 5-*dicarboxylate*, b.p. 143°/3 mm. (*Cu* derivative, m.p. 200°), and a substance, m.p. 82°, which does not form a Cu compound. H. W.

Lichen substances. LXVI. Constitution of lobaric acid. II. Y. Asahina and M. Yasue (Ber., 1936, 69, [*B*], 643—649; cf. A., 1935, 1366).—Thermal decomp. of lobaric acid (I) at 200—300°/1 mm. affords *lobaritonide* (II), m.p. 127—128°, n-*amylquinol* (III), m.p. 87°, and an impure material, m.p. 70—75°, which resembles 2 : 3 : 5-trihydroxy-1-methyl- or -1 : 4-dimethyl-benzene in its behaviour towards NH_3 and $CaOCl_2$ in EtOH. (II) gives a *Me ether*, m.p. 99°, oxidised by $KMnO_4$ in $COMe_2$ to 3 : 5-dimethoxyphthalic anhydride and Pr^aCO_2H. Hydrolysis of (II) by conc. HCl in $COMe_2$ at 50° gives *lobaritonic acid*, $C_{13}H_{16}O_5$, m.p. 120°, converted by N_2H_4,H_2O or $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ in EtOH into the *hydrazone anhydride*, $C_{13}H_{16}O_3N_2$, m.p. 151°; the corresponding *Me_1 ether*, m.p. 134,° is decarboxylated in quinoline containing Cu-bronze at 215° to 3 : 5-dimethoxyvalerophenone, m.p. 42·43°. (II) has therefore the constitution shown. (III) is oxidised by HNO_3 in AcOH to n-*amyl*-p-*benzoquinone*, m.p. 22°, and is obtained synthetically by reducing (Zn–Hg and HCl) 2 : 5-*dihydroxyvalerophenone*, b.p. 161—163°/4 mm. (*semicarbazone*, m.p. 189—190°), obtained from Bu^aCO_2H and *m*-$C_6H_4(OH)_2$ in presence of $ZnCl_2$. Lobariol (IV) is converted by reduction with Na–Hg and subsequent acidification into *lobariolide* (V), $C_{24}H_{30}O_6$, m.p. 87° after softening at 83°, or $(+1H_2O)$, m.p. (indef.) about 75°. *Lobariol Me_2 ether*, m.p. about 138°, from (IV), Me_2SO_4, and NaOH, is reduced by Na–Hg to *lobariolide Me_2 ether*, also obtained from (V) and CH_2N_2, which is oxidised by $Na_2Cr_2O_7$ in AcOH to the quinone (VI), $C_{25}H_{30}O_7$, m.p. 139°, obtained previously (*loc. cit.*) from permethylated norlobariolide; 6-methoxy-2-*n*-amyl-*p*-benzoquinone, b.p. 163°/3 mm., m.p. 1·3°, is also obtained. Reduction of (VI) with H_2SO_3 affords the colourless *quinol*, m.p. 151—152° (*diacetate*, m.p. about 100° after softening at 80°). The structure *A* is assigned to (I). H. W.



(II.)



(*A*.)

Oxidation of acetaldehyde and benzaldehyde by hydrogen peroxide in presence of selenium oxychloride. J. B. Firth and H. H. Gething (J.C.S., 1936, 633—634).—Oxidation of MeCHO or PhCHO to the acids by H_2O_2 is greatly accelerated by addition of $SeOCl_2$ (max. at 0·1—0·2 c.c. per 0·5 g. MeCHO) and by rise of temp. HCl alone does not catalyse the oxidation. J. W. B.

Catalytic hydrogenation of nitriles with nickel. Hydrogenation of hydroxybenzonitriles and their methyl ethers. H. Rupe and W. Brentano (Helv. Chim. Acta, 1936, 19, 588—596).—The yield of aldehyde obtained in the hydrogenation (Ni) of nitriles in $EtOAc–EtOH–H_2O$ is increased by the presence of $NHPh{\cdot}NH_2$, although the rate of reaction is greatly reduced. Some of the aldehyde is obtained free and some as phenylhydrazone; much NH_2Ph is formed. *p*- and *o*-$OH{\cdot}C_6H_4{\cdot}CN$ (I) and *p*- and *o*-$OMe{\cdot}C_6H_4{\cdot}CN$ give 40·66, 40, 14·66, and 40·5%, respectively, of aldehyde without and 54·25, 50, 27·33, and 66%, respectively with $NHPh{\cdot}NH_2$. *Di*-p- and -o-*methoxybenzylamine* have m.p. 35—37°, b.p. 225—230°/10 mm., and b.p. 200—210°/10 mm., respectively. o-*Methoxybenzylamine* has b.p. 120—125°/10 mm. The prep. of (I) from *o*-$OH{\cdot}C_6H_4{\cdot}NO_2$ by way of the *p*-$C_6H_4Me{\cdot}SO_2$ derivative, reduction by Fe–AcOH, hydrolysis, and Sandmeyer reaction is impracticable owing to poor yields in the last reaction. R. S. C.

Conversion of acids into aldehydes. J. S. McFadyen and T. S. Stevens (J.C.S., 1936, 584—587).—Benzenesulphonylacylhydrazides are prepared thus: (*a*) $R{\cdot}CO_2H \rightarrow R{\cdot}CO_2Et \rightarrow R{\cdot}CO{\cdot}NH{\cdot}NH_2 + PhSO_2Cl + C_5H_5N \rightarrow R{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}SO_2Ph$ (I) or (*b*) $R{\cdot}COCl + PhSO_2{\cdot}NH{\cdot}NH_2 + C_5H_5N \rightarrow$ (I): (*a*) is better since (*b*) favours diacylation and thus *benzenesulphondibenzoylhydrazide*, m.p. 198—200° (decomp.), is obtained. The following are prepared usually by method (*a*): *benzenesulphonyl-benzoyl-*, m.p. 192—194° (decomp.), -o-*hydroxy-*, m.p. 161—162°, -p-*methoxy-*, m.p. 187—189° (decomp.), -3 : 4-*methylenedioxy-*, m.p. 166—168°, -m-, m.p. 222—223° (decomp.), and -p-*nitro-benzoyl-*, m.p. 197—199° (decomp.), -iso*butyryl-*, m.p. 156—158°, and -*diphenylacetyl-*, m.p. 191—193°, -*hydrazide*; 2 : 5-*dichlorobenzenesulphonyl-benzoyl-*, m.p. 186—188° (decomp.), -p-*chlorobenzoyl-*, m.p. 235—237° (decomp.), and -o-*hydroxybenzoyl-*, m.p. 229—230° (decomp.), -*hydrazide*. Cinnamoylhydrazide and $PhSO_2Cl$ give a *compound*, m.p. 169—171° (decomp.). Addition of alkali to a solution of (I) in hot glycol affords good yields (42—87%) of aromatic aldehydes: (I) → $PhSO_2K+(R·CO·N:NH) \rightarrow R·CHO+N_2$, but fails in the aliphatic series. The yield is best when a considerable excess of alkali (best Na_2CO_3) at 160° is used, and is unaffected by the quantity of solvent: prolonged heating (>75 sec.) gives poor results. The reaction can be applied to the replacement of reactive halogen in the benzene ring by H; thus picryl chloride and $PhSO_2·NH·NH_2$ afford *benzenesulphon-2′ : 4′ : 6′-trinitrophenylhydrazide*, m.p. 210—220° (decomp.), which gives 1 : 3 : 5-$C_6H_3(NO_2)_3$, and the -2′ : 4′-*dinitrophenylhydrazide*, dimorphous, laminæ and needles, both m.p. 196—198° (decomp.), gives *m*-$C_6H_4(NO_2)_2$. *Piperonoylhydrazide* has m.p. 171—172°. J. W. B.

Derivatives of *p*-homosalicylaldehyde. K. CHANG and P. P. T. SAH (J. Chinese Chem. Soc., 1936, 4, 80—83).—*p*-Homosalicylaldehyde (5-methyl-2-hydroxybenzaldehyde; cf. A., 1878, 875) with hydrazines or semicarbazides in boiling 95% EtOH affords cryst. derivatives. The following are prepared: *phenyl-*, m.p. 148·5—149·5°, o-, m.p. 149—150° and p-*tolyl-*, m.p. 153·5—155·5°, and β-*naphthylhydrazone*, m.p. 201·5—202·5°; o-*nitro-*, m.p. 232—233°, and 2-*bromo*-4-*methyl-phenylhydrazone*, m.p. 128—129°; 3-, m.p. 253—254° (uncorr.), 4-*nitro-*, m.p. 269—270°, 3 : 5-*dinitro-*, m.p. 259·5—260·5°; p-*chloro-*, m.p. 247—248° (decomp.), and p-*bromobenzoylhydrazone*, m.p. 246·5—247·5°; o-, m.p. 208—209°, and p-*tolylsemicarbazone*, m.p. 212—213°. J. L. D.

Theory and practice of the halogenation of active methyl and methylene groups. F. KRÖHNKE (Ber., 1936, 69, [*B*], 921—935; cf. this vol., 592).—When Br (1 mol.) acts on COPhMe in 15 different media and the action is interrupted immediately after disappearance of the colour of the halogen the proportions of $COPh·CH_2Br$, $COPh·CHBr_2$, and COPhMe in the product vary with the solvent; if the reaction is interrupted after a further 1·5—2 hr. the ratio $COPh·CH_2Br : COPh·CHBr_2$ (80 : 20) is independent of the medium. Similar observations are recorded for other Me ketones, the constitution of which controls the position of equilibrium. For max. utilisation of Br in production of monobromo-ketones it is necessary to use an excess of ketone; AcOH, CCl_4, and CS_2 are unsuitable as media since in them the " time equilibrium " is very rapidly established whereas $CHCl_3$ and EtBr are well adapted to the purpose. HBr activates the Me and CH_2Br ketone and also has a dehalogenating action, thus:

$$\cdot COMe(+H) \rightarrow \cdot C(OH){:}CH \rightleftharpoons (+Br)$$
$$\cdot CBr(OH)\cdot CH_2Br \rightleftharpoons \cdot CO\cdot CH_2Br \rightleftharpoons (+HBr)$$
$$\cdot C(OH){:}CHBr \rightleftharpoons (+Br)\ \cdot CBr(OH)\cdot CHBr_2 \rightleftharpoons$$
$$\cdot CO\cdot CHBr_2.$$

There is no apparent relationship between the effect of medium and its physical nature. Since further bromination of CHBr ketones is difficult, the equilibrium is generally in favour of the Br_1 compound. The CBr_2 ketones in presence of HBr readily and almost completely undergo the change, *e.g.*, $COPh·CMeBr_2+COPhEt \rightarrow 2COPh·CHMeBr$ and analogously the CBr_3 compounds give the reaction $COPh·CBr_3+2COPhMe \rightarrow 3COPh·CH_2Br$. Unexpectedly bromination of COPhMe in presence of KOAc (as catchment for HBr) is accompanied by production of more $COPh·CHBr_2$ than in its absence; owing to non-activation of COPhMe by acid the reaction necessitates a higher temp. whilst $COPh·CH_2Br$ is regarded as activated by HBr in its immediate vicinity previous to the reaction with KOAc. $CaCO_3$ behaves similarly. Bromination is preceded by the formation of red additive compounds, *e.g.*, $CORMe,Br_2$. The separation of mono- and di-bromoketones is effected by C_5H_5N in hot EtOH in which the former rapidly produce salts, $COR·CH_2·N(C_5H_5)Br$ whereas the latter react only after expulsion of EtOH at 100° thus: $COR·CHBr_2+2C_5H_5N+H_2O = R·CO_2H+CH_2(NC_5H_5Br)_2$. The following appear new: ω-*tribromoacetophenone*, m.p. 65—66°, b.p. 176°/16 mm.; *pinacolinylpyridinium bromide*, m.p. 203—204°; 3-*phenanthracylpyridinium bromide*, m.p. 233° (decomp.); 4 p-*chlorophenacylpyridinium bromide*, m.p. 206° (decomp.) after softening at 203°, and the corresponding *enolbetaine* $C_{13}H_{10}ONCl$, m.p. 135—136° (decomp.) after becoming discoloured at 132°; 3 : 4-*dichlorophenacylpyridinium bromide*, m.p. 222° (decomp. commencing at 220°), and the *enolbetaine* $C_{13}H_9ONCl_2$, m.p. 130—135° (decomp.); p-*iodophenacylpyridinium bromide*, m.p. 252—253° (decomp. beginning at 248°), and the *enolbetaine* $C_{13}H_{10}ONI$, m.p. 147° (decomp.) after becoming discoloured at 140°; m-*nitrophenacylpyridinium bromide*, m.p. 244—245° (decomp.), and the corresponding *picrate*. H. W.

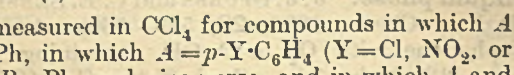
Halogen analogues of adrenaline and ephedrine. II. Derivatives of acetophenone. R. P. EDKINS and W. H. LINNELL (Quart. J. Pharm., 1936, 9, 75—109; cf. A., 1932, 1245).—3-*Amino*-4-*hydroxyacetophenone* (an oil) obtained by reduction of the 3-NO_2-derivative gave 3-*bromo*-4-*hydroxyacetophenone* (I), m.p. 112°, by the Sandmeyer method. (I) in Et_2O saturated with HCl gave with $BuNO_2$ the *oximino*-derivative, and reduction *in situ* with $SnCl_2$ gave 3-*bromo*-ω-*amino*-4-*hydroxyacetophenone hydrochloride*, m.p. 236°. In a similar way the *hydrochloride*, m.p. 235°, of the 3-Cl-derivative was obtained. 3-*Chloro*-5-*nitroso*-4-*hydroxyacetophenone*, m.p. 110°, was obtained from the chlorohydroxyketone and $BuNO_2$ in AcOH. The *hydrochlorides* of 3-chloro-, 3-bromo-, 4-chloro-, and 4-bromo-ω-aminoacetophenones, m.p. 222°, 236°, 290°, and 306°, respectively, were obtained by reduction of the corresponding -oximino-compounds with $SnCl_2$ in Et_2O saturated with HCl. Reduction of these halogenated ω-aminoacetophenones in aq. solution with H_2 (Pd) gave excellent yields of $OH·CHPh·CH_2·NH_2,HCl$, halogen being eliminated, whilst in EtOH with or without H_2, but in presence of Pd, hydrolysis occurred, and theoretical yields of the halogenobenzoic acids were obtained. J. N. A.

4-Chloroacetophenone. Catalytic oxidation in the liquid phase. J. J. STUBBS and C. E. SENSEMAN (Ind. Eng. Chem., 1936, 28, 559—560).—4-Chloroacetophenone with O_2 in AcOH containing MnO_2 at 110—112° during 3 hr. affords 91% *p*-$C_6H_4Cl·CO_2H$ (I). In the absence of MnO_2 no (I) is formed. J. L. D.

Organo-magnesium derivative of pentamethylbenzene. H. Clément (Compt. rend., 1936, **202**, 425—427; cf. A., 1934, 526).—Xylene and MeCl in presence of $AlCl_3$ (24 hr.) afford an easily separable mixture of C_6HMe_5 and C_6Me_6. $C_6Me_5{\cdot}MgBr$ (I), prepared in presence of EtBr (*loc. cit.*), and AcCl yield *pentamethylacetophenone*, m.p. 110° (*oxime*; *semicarbazone*), and some *pentamethylphenylmethylethylcarbinol*, m.p. 52°. Similarly (I) (containing EtBr) with BzCl or EtOBz affords *pentamethylbenzophenone*, m.p. 125° (*oxime*; *semicarbazone*), and some *pentamethylphenylphenylethylcarbinol*, m.p. 49°, and with HCO_2Et affords *pentamethylbenzaldehyde*, m.p. 130·5° (*oxime*; *semicarbazone*). H. G. M.

***ar*-Turmerone from curcuma oil.** H. Rupe and A. Gassmann [with (in part) R. Haecker] (Helv. Chim. Acta, 1936, **19**, 569—581).—*ar*-Turmerone (I), *p*-$C_6H_4Me{\cdot}CHMe{\cdot}CH_2{\cdot}CO{\cdot}CH{:}CMe_2$, and dl-*dihydro*-ar-*turmerone* (II) are synthesised. Crude curcuma oils had $[\alpha]_D$ −9° to +7·54°, but various samples of rhizome gave to C_6H_6 only dextrorotatory mixtures, $[\alpha]_D$ +0·82° to +20·48°. The oil gave cryst. compounds with $H_4Fe(CN)_6$ and $H_3Fe(CN)_6$, but treatment with these reagents does not give pure products. Oxidation of the oil with Pd–C, Se, SeO_2, $FeCl_3$, and O_2–$FeCl_3$ gives oils enriched in (I), but pure (I), b.p. 159—160°/10 mm., $[\alpha]_D^{20}$ +82·21°, $[\alpha]_{5461}^{20}$ +101·06°, is best obtained by controlled oxidation with CrO_3, prep. of the *dinitrophenylhydrazone* (III), m.p. 133—134°, and hydrolysis thereof with hot HCl–EtOH. When pure, (I) gives a *semicarbazone*, m.p. 108—109°, an *oxime*, b.p. 179—180°/10 mm., and *hydroxylamino*-compound, m.p. 112° (stable to acid). (III), but not (I), with conc. acid may give *d*-curcumone (IV) (*dinitrophenylhydrazone*, m.p. 89·5°). Hydrogenation (Ni) of (I) in 70% EtOH gives *dihydro*-ar-*turmerone*, b.p. 146—147°/10 mm., $[\alpha]_D^{20}$ +44·25°, $[\alpha]_{5461}^{20}$ +54·3° (*dinitrophenylhydrazone*, m.p. 121—122°; *oxime*, b.p. 169—170°/10 mm.). (II), b.p. 145—155°/10 mm. (*dinitrophenylhydrazone*, m.p. 127—128°, not depressed by admixture with the *d*-compound; *oxime*, b.p. 169—170°/10 mm.), is best obtained from β-p-*tolylpropionpiperidide*, b.p. 205—208°/10 mm., and $MgBu^{\beta}I$, and, less well, from *p*-$C_6H_4Me{\cdot}CHMe{\cdot}CH_2{\cdot}COCl$ and $ZnBu^{\beta}I$ or $CPr^{\beta}Na(CO_2Et)_2$. (IV) and $COMe_2$ with cold NaOEt (not other reagents) gives (I). R. S. C.

Beckmann change. IV. Effects of substitution on the rate of rearrangement of ketoxime picryl ethers. Suggested mechanism of the transformation. A. W. Chapman and F. A. Fidler (J.C.S., 1936, 448—453; cf. A., 1935, 1498).—Velocities of Beckmann rearrangement of *p*-substituted benzophenoneoxime picryl ethers (I) (X=picryl) into the corresponding amides (III):



$$\begin{array}{c}A{\cdot}C{\cdot}B\\ \|\\ N{\cdot}OX\end{array} \longrightarrow \begin{array}{l}\;\;C\!<\!\begin{array}{l}B\\ OX\end{array}\\ A{\cdot}N\end{array} \longrightarrow \begin{array}{c}B{\cdot}C{:}O\\ |\\ A{\cdot}N{\cdot}X\end{array}$$

(I). (II). (III.)

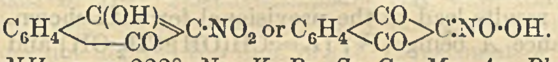
are measured in CCl_4 for compounds in which *A* and *B*=Ph, in which *A*=*p*-$Y{\cdot}C_6H_4$ (Y=Cl, NO_2, or Me) and *B*=Ph, and vice versa, and in which *A* and *B*=*p*-$Y{\cdot}C_6H_4$ (Y=Cl, NO_2, Me, or OMe). It is suggested that the activity of reagents promoting the Beckmann rearrangement of ketoximes depends on the formation of ethers of type (I) (X=acyl etc.), in which the change is spontaneous, its velocity depending on the polar character of the solvent. There is no evidence that ions are formed. The attraction for electrons exerted by ·OX creates a dipole at ·N·O, its positive end being at N. If the mol. acquires sufficient energy, N becomes attached to *A* and OX migrates. The process is facilitated by electron-repelling groups on *A* or *B*. The following are prepared. *Ph* p-*tolyl* α- and -β-*ketoxime picryl ethers*, m.p. 103° and 83°, converted respectively into p-*toluoyl*-N-*picrylanilide*, m.p. 209° [also obtained from *p*-toluanilideimidochloride and $C_6H_2(NO_2)_2{\cdot}ONa$], and *benz*-N-*picryl*-p-*toluidide*, m.p. 180—185° (also obtained from benz-*p*-toluidideimidochloride). p-*Nitrobenzophenone-α-oxime picryl ether*, m.p. 134°, when heated in $(CH_2Cl{\cdot})_2$ for 5 hr. at 100° gives p-*nitrobenz*-N-*picrylanilide*, m.p. 214—215°; the β-*oxime picryl ether*, m.p. 154—155°, is unchanged under the same conditions. The *picryl ether*, m.p. 189°, of pp′-*dinitrobenzophenoneoxime*, m.p. 195° (decomp.), is similarly unchanged, as is *benzophenoneoxime* 2 : 4-*dinitrophenyl ether*, m.p. 173—174°; the isomeric *benz*-N-2 : 4-*dinitrophenylanilide*, m.p. 155—156°, is obtained from benzanilideimidochloride and Na 2 : 4-dinitrophenoxide. *p*-Chlorobenzophenone-β-oxime picryl ether has m.p. 116—118° (cf. A., 1933, 952). Attempts to prepare di-*p*-anisylketoxime picryl ether, even in a freezing mixture, give *p*-anisoyl-*p*-anisidide. Improved methods of separating isomeric *p*-chloro- and *p*-methyl-benzophenoneoximes are described. E. W. W.

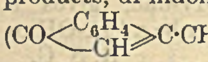
Action of alkalis on aromatic ketones. N. S. Kozlov, P. N. Fedoseev, and L. E. Olifson (J. Gen. Chem. Russ., 1936, **6**, 259—264).—Ketones of the type $C_6H_4R{\cdot}COPh$ decompose when heated at 250—300° for 50 min. with KOH, to yield $C_6H_4R{\cdot}CO_2H$+C_6H_6, whilst with $C_6H_3R_2{\cdot}COPh$ the products are $C_6H_4R_2$ and BzOH. Thus *o*- and *p*-$C_6H_4Et{\cdot}COPh$ yield *o*- and *p*-$C_6H_4Et{\cdot}CO_2H$ and C_6H_6, *p*-$C_6H_4Pr^{\beta}{\cdot}COPh$ affords *p*-$C_6H_4Pr^{\beta}{\cdot}CO_2H$ (I) and C_6H_6, 4 : 4′-*di*iso*propylbenzophenone*, b.p. 195—196°/1 mm. (from $PhPr^{\beta}$ and $COCl_2$ in presence of $AlCl_3$), gives (I) and $PhPr^{\beta}$, and 4 : 4′-*diethylbenzophenone*, b.p. 344° (from PhEt, $COCl_2$, and $AlCl_3$), yields *p*-$C_6H_4Et{\cdot}CO_2H$ and PhEt, whilst 2 : 4-*di*iso*propylbenzophenone*, b.p. 334—335° [from *m*-$C_6H_4Pr^{\beta}_2$ (II) and BzCl, in presence of $AlCl_3$], gives (II) and BzOH, and $C_6H_3MePr^{\beta}{\cdot}COPh$ yields $C_6H_3MePr^{\beta}{\cdot}CO_2H$, BzOH, C_6H_6, and *p*-cymene. R. T.

Synthetical experiments with benzhydrylsodium. E. Bergmann (J.C.S., 1936, 412—413; cf. A., 1930, 1585).—$CHPh_2Na$ usually undergoes 1 : 4-addition to Δ^{α}-unsaturated CO-compounds. $CPh{:}C{\cdot}CO_2Et$, however, gives a carbinol, *γ-phenyl-αα-bis(diphenylmethyl)propargyl alcohol*, m.p. 178—179°. $CHPh_2Na$ reacts with enolisable esters partly in the normal way, and partly is converted into CH_2Ph_2 by the enolic form. Acyl chlorides of corresponding type react exclusively in the enolic form. $CHMeBr{\cdot}CO_2Et$ condenses normally, forming *ααδδ-tetraphenyl-γ-methylbutan*-β-*one*, m.p. 130—131° (hydrolysed to ββ-*diphenyl*iso*butyric acid*, m.p. 160—

161°). With Et fluorene-9-carboxylate, the enolic reaction prevails, giving CH_2Ph_2. The condensation product with $CPh_3\cdot COPh$ decomposes spontaneously into $CHPh_3$ and $COPh\cdot CHPh_2$. The following are also prepared. From $CH_2Ph\cdot CH_2Cl$, $CH_2Ph\cdot CH_2\cdot CHPh_2$; from CHPhMeCl, $CHPhMe\cdot CHPh_2$; from $CH_2Cl\cdot OMe$, $CHPh_2\cdot CH_2\cdot OMe$; from CH_2O, $CHPh_2\cdot CH_2\cdot OH$; from $COMe_2$ or $CO(CH_2Ph)_2$, CH_2Ph_2; from $(COPh)_2$, $(CHPh_2)_2$ and $COPh\cdot CHPh\cdot OH$; from $COPh\cdot CHPh\cdot OEt$, α-*ethoxy*-αβγγ-*tetraphenylpropan*-β-*ol*, m.p. 140°; from benzylideneacetophenone oxide, γδ-*epoxy*-ααβδ-*tetraphenylbutan*-β-*ol*, m.p. 179—180°; from p-$C_6H_4Cl\cdot COMe$, ββ-*diphenyl*-α-p-*chlorophenylethanol*, m.p. 176—178°, dehydrated (AcCl) to p-*chlorotetraphenylethylene*, m.p. 166—167° (cf. Norris and Tibbetts, A., 1920, i, 831); from (*p*-$C_6H_4Cl)_2CO$, ββ-*diphenyl*-αα-*bis*-(p-*chlorophenyl*)*ethanol*, m.p. 183—184°, dehydrated (AcCl) to an anomalous *product*, $C_{26}H_{20}O_3Cl_2$, m.p. 185—186°; from (*p*-$C_6H_4Br)_2CO$, ββ-*diphenyl*-αα-*bis*-(p-*bromophenyl*)-*ethanol*, m.p. 197°, dehydrated to pp′-*dibromotetraphenylethylene*, m.p. 205°; from *p*-$OMe\cdot C_6H_4\cdot COPh$, αββ-*triphenyl*-α-p-*anisylethanol*, dehydrated to p-*methoxytetraphenylethylene*, m.p. 131—132°; from CHPh:$CH\cdot COMe$, CH_2Ph_2 and *Me* βγγ-*triphenyl*-n-*propyl ketone*, m.p. 137°; from CHPh:$CH\cdot COPh$, *Ph* βγγ-*triphenyl*-n-*propyl ketone*, m.p. 182—184°; from *p*-$OMe\cdot C_6H_4\cdot CH{:}CH\cdot COPh$, *Ph* γγ-*diphenyl*-β-p-*anisyl*-n-*propyl ketone*, m.p. 146—148°; from $CHPh{:}CH\cdot CH{:}CH\cdot COPh$, *Ph* δ-*phenyl*-β-*benzyl*-Δ^{γ}-*butenyl ketone*, m.p. 151—152°; from $CPh_2{:}N\cdot NPhMe$, N-*phenyl*-N′-ααββ-*tetraphenylethyl*-N-*methylhydrazine*, m.p. 149—151°, with some $(CHPh_2)_2$; from $CH_2Ph\cdot OBz$ or PhCN, $CHPh_2\cdot COPh$; from *o*-$OMe\cdot C_6H_4\cdot CO_2Et$, o-*anisyl benzhydryl ketone*, m.p. 86—87°; from *o*-$C_6H_4F\cdot CO_2Me$, o-*fluorophenyl benzhydryl ketone*, m.p. 84—85°; from AcCl or $CH_2Ph\cdot COCl$, CH_2Ph_2; from $Pr^{\beta}CO_2Et$, CH_2Ph_2 and *benzhydryl* iso*propyl ketone*, m.p. 75—76°; from $CH_2Ph\cdot CHMe\cdot CO_2Et$, CH_2Ph_2 and *benzhydryl* β-*phenyl*iso*propyl ketone*, b.p. 250—252°/16 mm.; from $(CH_2Ph)_2CH\cdot CO_2Et$, CH_2Ph_2 and *benzhydryl* β-*phenyl*-α-*benzylethyl ketone*, m.p. 107—108°; and from $CHPh{:}CH\cdot CO_2Me$, *Me* βγγ-*triphenylbutyrate*, m.p. 126—127°. E. W. W.

Action of amines on indandione derivatives. G. Wanag and V. Walbe (Ber., 1936, **69**, [*B*], 1054—1060).—2-Phenylindan-1 : 3-dione (I) and NH_2Ph in boiling EtOH give 1-*anilo-2-phenylindan-3-one*, m.p. 212—213°, hydrolysed by boiling 2*N*-HCl to (I) and NH_2Ph,HCl. The following 2-*phenylindan-3-ones* are obtained similarly: -1-p-*tolylimino*-, m.p. 242°, identical with the "phenylindandionetoluidide" of Liebermann; -1-p-*anisylimino*-, m.p. 239—240°; -1-2′-*naphthylimino*- (II), m.p. 274—275° (block). 2-Methylindan-1 : 3-dione and NH_2Ph afford 1-*anilo-2-methylindan-3-one* (III), m.p. 153°. The compounds are generally stable towards H_2O_2 in boiling EtOH with the exception of (III), which is slowly transformed into phthalanil. 2-Bromo-2-phenylindan-1 : 3-dione and *p*-$C_6H_4Me\cdot NH_2$ in boiling EtOH yield 2-p-*toluidino-2-phenylindan*-1 : 3-*dione*, m.p. 187°. *p*-$OMe\cdot C_6H_4\cdot NH_2$ similarly affords 2-p-*anisidino-2-phenylindan*-1 : 3-*dione*, m.p. 165°, whereas β-$C_{10}H_7\cdot NH_2$ affords 2-2′-*naphthylimino-2-phenylindan*-1 : 3-*dione*, m.p. 201—203°, and some (II). 2-Anilino-2-phenylindan-1 : 3-dione is converted by $NaNO_2$ and HCl into *nitroso-2-anilino-2-phenylindan*-1 : 3-*dione*, m.p. 187°. 2-*Methylanilino-2-phenylindan*-1 : 3-*dione* has m.p. 119°. Condensation with aliphatic amines is effected in Et_2O. Thus are obtained 2-iso*butylamino*-, m.p. 95°; 2-*propylamino*-(*hydrochloride*, decomp. 239°; *nitroso-2-propylamino-2-phenylindan*-1 : 3-*dione*, m.p. 139—140°; *propylammonium bromide*, m.p. 182°); 2-*ethylamino*- [*hydrochloride*, m.p. 237° (decomp.)]; 2-*methylamino*- (*hydrochloride*, decomp. 235°), -2-*phenylindan*-1 : 3-*dione*. 2-Anilino-2-methyl*indan*-1 : 3-*dione* has m.p. 190°. H. W.

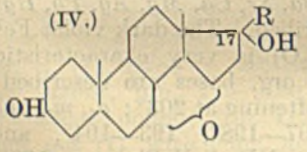
2-Nitroindan-1 : 3-dione and its salts. G. Wanag (Ber., 1936, **69**, [*B*], 1066—1074).—Indan-1 : 3-dione is transformed by fuming HNO_3 in AcOH into *o*-$C_6H_4(CO_2H)_2$ (I). If the experiment is performed with efficient cooling 2-*nitroindan*-1 : 3-*dione* (II), m.p. 110°, or ($+2H_2O$), m.p. 113° (decomp.), is obtained in 78% yield. It is converted by conc. NaOH or conc. H_2SO_4 into (I) and NH_3 (derived from $MeNO_2$). (II) and Br–H_2O afford 2-*bromo-2-nitroindan*-1 : 3-*dione*, m.p. 115—116°. (II) is a about as strong as HCl and hence in solution exists in the form,  $C_6H_4{<}\begin{matrix}C(OH)\\CO\end{matrix}{\geqslant}C\cdot NO_2$ or $C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C{:}NO\cdot OH$. The *$NH_4$*, m.p. 222°, *Na*, *K*, *Ba*, *Sr*, *Ca*, *Mg*, *Ag*, *Pb*, *Hg^{I}*, *Cd*, and *Cu* salts are described. The dark violet Fe^{II} salt ($+4H_2O$ and $+2H_2O$) is very characteristic. *Salts* from the following org. bases are described: NH_2Ph, m.p. 209° after softening at 203°; *o*-, *m*-, and *p*-$C_6H_4Me\cdot NH_2$, m.p. 197—198°, 193—194°, and 192—193°, respectively; *p*-$NH_2\cdot C_6H_4Ph$, m.p. 199°; NHPhMe, m.p. 186°; $NPhMe_2$, m.p. 133°. (II) appears suitable for the isolation and characterisation of org. bases, thus resembling picric, picrolonic, and styphnic acid; the group $OH\cdot C{:}C\cdot NO_2$ or $O{:}C\cdot C{:}NO\cdot OH$, which readily forms an internal complex, is common to all. H. W.

Condensation of indan-1 : 3-dione with acetone. A. Cirulis (Annalen, 1936, **522**, 278—284).—Indan-1 : 3-dione (I) and $COMe_2$+piperidine give resinous products, di-indone, and s-*di*-(3-*indenonyl*)*acetone* (II),  $(CO{<}\begin{matrix}C_6H_4\\CH\end{matrix}{\geqslant}C\cdot CH_2)_2CO$, m.p. 199—200° [*Na*, *Ag*, and *Ba* salts; *Me_2*, m.p. 251° (from MeI and MeOH–NaOMe), and *Br_2*-, m.p. 195°, derivatives; *monoxime*, m.p. 216° (decomp.); *tri*(*phenylhydrazone*), m.p. 248—249° (decomp.); *nitrate*, m.p. 233—235° (decomp.; evolution of NO), converted by MeOH–NaOMe into (II)]. (II) contains 2 active CH_2 groups and 2 enolisable H; it exists in yellow (keto) and bluish-green (enol) forms. (II) is produced by elimination of $2H_2O$ from 2 mols. of the enolic form of (I) and 1 mol. of $COMe_2$. The di-indandionylpropane of Radulescu and Georgescu (A., 1925, i, 1285) is impure (II). The presence of a little $COMe_2$ in COMeEt is demonstrated by treatment with (I) (as above); (II) is isolable. H. B.

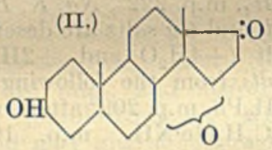
Dimesityl diketones and their derivatives. III. αη-Dimesitylheptane-αη-dione and βζ-dibromo-αη-dimesitylheptane-αη-dione. T. Y. Kao and C. K. Chang (J. Chinese Chem. Soc., 1936, 4, 103—104).—*αη-Dimesitylheptane-αη-dione*, m.p. 72—73·5° (βζ-*Br*$_2$-derivative, m.p. 132—134°), is synthesised from pimelic acid (cf. A., 1935, 862). J. L. D.

Constituents of the adrenal gland. IV. T. Reichstein (Helv. Chim. Acta, 1936, **19**, 402—412; cf. this vol., 704).—Substances *A*, *C*, and *D* with CrO_3 give a *diketone* (I), $C_{19}H_{26(28)}O_3$, m.p. 178—180° (corr.), sublimes at 165°/0·1 mm. [*dioxime*, m.p. 274—276° (corr.; decomp.), sublimes at about 220—250°/high vac.], and are thus closely related. Substance *E* is probably of a different type, since with CrO_3 it gives a *substance* (possibly impure), m.p. 211—216° (corr.), sublimes at 180°/0·1 mm. Substance *A* absorbs 2·5 O from $Pb(OAc)_4$, giving a *ketone* (II), $C_{19}H_{28-30}O_3$, m.p. 235—238° (corr.), $[\alpha]_D^{20}$ +84·5±3° in dry EtOH [*semicarbazone*, m.p. 317—322° (corr.; decomp.), hygroscopic], and an *acid*, $C_{18}H_{30}O_2(CO_2H)_2$, m.p. 256—258° (corr.; decomp.); it absorbs 2 O from KIO_3 to give (II) only. (II) with a little CrO_3 gives a *substance* (possibly impure) (III), $C_{19}H_{28}O_3$, m.p. 156·5—158° (corr.), sublimes at 180—190°/0·02 mm. [*dioxime*, m.p. 262—273° (decomp. from 230°)], oxidised by CrO_3 to (I), which is also obtained directly from (II) by more CrO_3. (II) is pptd. by digitonin in 90% EtOH, confirming its relation to *trans*-androsterone. These results lead to the provisional formulæ shown, substance *A* being (IV) [R=·CH(OH)·CH_2·OH] and substances *C* and *D* stereoisomerides of (IV) (R=CO·CH_2·OH) with respect to $C_{(17)}$. These relations are strengthened by the fact that (II), (I), and (III) have one thirtieth, third, and seventh, respectively, of the activity of androsterone by the capon test. The sensitivity of the digitonin test is greater in 50% MeOH than in 90% EtOH; in 50% MeOH androstanedione, but not 3-*epi*hydroxyætiocholan-17-one, gives a ppt. The O in the formulæ given may be a *tert.*-OH or ethereal. R. S. C.

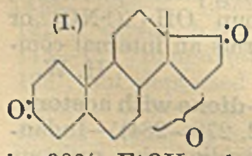
(IV.)



(II.)



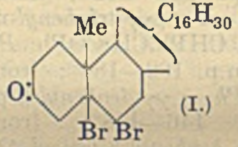
(I.)



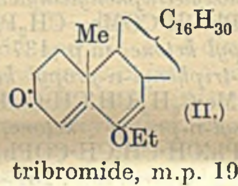
Synthesis of Δ⁴-dehydroandrosterone (3-hydroxy-Δ⁴-ætiocholen-17-one) directly from cholesterol. I. A. Remesov (Compt. rend. Acad. Sci. U.R.S.S., 1936, **1**, 261—263).—Cholesteryl acetate dibromide is converted by oxidation with CrO_3 and subsequent reduction and hydrolysis into Δ⁴-*dehydroandrosterone*, m.p. 144—146°, which exhibits high biological activity (cocks). J. W. B.

Δ¹-Androstene-3 : 17-dione. A. Butenandt and H. Dannenberg (Ber., 1936, **69**, [*B*], 1158—1162).—Androstanedione is transformed by Br in AcOH–HBr into 2-*bromoandrostandione*, m.p. 213—214° (decomp.), converted by KOAc in AcOH at 200° into Δ¹-*androstene*-3 : 17-*dione* (I), m.p. 139—140°, $[\alpha]_D^{20}$ +6·8° in EtOH [*dioxime*, gradual decomp. 225—252°). The absorption spectrum of (I) proves the double linking to be in conjugation with CO, and further evidence in favour of the assigned constitution is obtained as follows. *iso*Androstanediol diacetate is partly hydrolysed to the 17-*monoacetate*, m.p. 147—148°, oxidised by CrO_3 in AcOH to *androstan*-17-*ol*-3-*one acetate*, m.p. 156—157°. This is hydrolysed to androstan-17-ol-3-one, m.p. 178°, transformed by Br in AcOH into 2-*bromoandrostan*-17-*ol*-3-*one*, m.p. 180—181° (decomp.), oxidised to (I). (I) has physiological activity similar to that of the follicular hormone. H. W.

Peculiar mode of formation of Δ⁴:⁵-cholestene-3 : 6-dione ethyl ether. H. H. Inhoffen (Ber., 1936, **69**, [*B*], 1134—1139).—Treatment of cholesterol with Br followed by oxidation of the product with CrO_3 in AcOH gives the *ketone dibromide* (I), decomp. 68—69°, debrominated to cholestenone. (I) and Br in Et_2O–AcOH at 20° afford the *bromoketone dibromide*, $C_{27}H_{43}OBr_3$, decomp. 137—138°, which when boiled with abs. EtOH under defined conditions passes into Δ⁴:⁵-cholestene-3 : 6-dione Et ether (II), m.p. 164—165°, hydrolysed by boiling AcOH containing $Zn(OAc)_2$ to cholestenedione. (II) and Br in $CHCl_3$–AcOH yield cholestenedione tribromide, m.p. 192—193° (decomp.). The mode of formation and inability of (II) to react with maleic anhydride at 140° suggest the annexed formula for it. H. W.



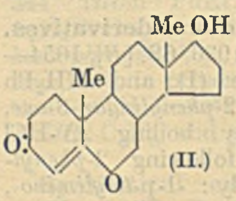
(I.)



(II.)

Absorption spectra of œstrone and related compounds.—See this vol., 776.

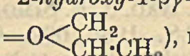
6-Ketotestosterone and related compounds. A. Butenandt and B. Riegel (Ber., 1936, **69**, [*B*], 1163—1168).—Oxidation of androstenediol monoacetate with CrO_3 (≡6 O) in AcOH yields 6-*ketotestosterone acetate* (I), m.p. 198—201°, $[\alpha]_D^{22}$ +47·2°±1·4° in $COMe_2$, and (?) *androstane*-5 : 17-*diol*-3 : 6-*dione* 17-*monoacetate*, m.p. 239—241° after softening at 229—231°, $[\alpha]_D^{22}$ −29·9°±1·3° in $COMe_2$. Cautious treatment of (I) with HCl–MeOH affords 6-*ketotestosterone* (II), m.p. 203—205°, $[\alpha]_D^{22}$ −58° in $COMe_2$. Dehydroandrosterone is oxidised to Δ⁴-*androstene*-3 : 6 : 17-*trione* (III), m.p. 216—217°, $[\alpha]_D^{22}$ +42·1°±1·4° in $COMe_2$ [*trioxime*, m.p. 235—237° (decomp.) after softening at 188°], an *acid*, m.p. 239—241°, $[\alpha]_D^{23}$ −12·5° in $COMe_2$, and (?) *androstan*-5-*ol*-3 : 6 : 17-*trione*, m.p. 248—249° after becoming discoloured at 225°, $[\alpha]_D^{23}$ +54·6° in $COMe_2$. The physiological activity of the original materials is so changed by the introduction of a further CO in conjugation with the double linking that (II) and (III) resemble the members of the œstrone group. H. W.

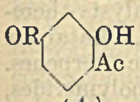


(II.)

Action of acetic anhydride on 2-acetylresorcinol. Synthesis of γ-resorcylic acid. D. B. Limaye and G. R. Kelkar (J. Indian Chem. Soc., 1935, **12**, 788—790).—2-Acetylresorcinol (cf. A., 1934,

298) with Ac_2O at 140—150° (3 hr.) gives the *diacetate*, b.p. 175—180°/10 mm., but with Ac_2O–NaOAc at 160° (5 hr.) gives *5-hydroxy-3-acetyl-2-methylchromone* (I), m.p. 122° (*Ac* derivative, m.p. 109°), together with a trace of a *compound*, m.p. 261—262°, probably the corresponding coumarin. γ-Resorcylic acid is obtained in good yield by hydrolysis of (I) with 0·5*N*-NaOH for 0·5 hr. H. G. M.

Glycerol ethers of resacetophenone. D. R. Nadkarni and T. S. Wheeler (J.C.S., 1936, 589—591).—Resacetophenone (I) and glycerol α-chlorohydrin with aq. KOH at 100° afford *2-hydroxy-4-(βγ-dihydroxypropoxy)acetophenone* [*A* ; R= OH·CH_2·CH(OH)·CH_2], m.p. 88° (*hydrazone*, m.p. 98°; *azine*, m.p. 292—294°; *phenylhydrazone*, m.p. 119—120°), and *glycerol αγ-bis-(3-hydroxy-4-acetylphenyl) ether*, m.p. 161° (*hydrazone*, m.p. 184°; *azine*, m.p. > 300°; *phenylhydrazone*, m.p. 206°), the proportion of which is increased by use of higher [KOH]. (I) and epichlorohydrin with aq. NaOH at room temp. give *2-hydroxy-4-βγ-epoxypropoxyacetophenone* (II) (*A* ;  $R{=}O{<}\begin{matrix}CH_2\\CH{\cdot}CH_2\end{matrix}$), m.p. 78° (*Ac* derivative, m.p. 198—200°), and (?) 2 : 4-bis-(βγ-epoxypropoxy)acetophenone (azine, m.p. > 300°) which could not be purified. When only a trace of 10% NaOH is used as a catalyst *2-hydroxy-4-γ-chloro-β-hydroxypropoxyacetophenone*, $+H_2O$, (III), m.p. 68° (softens 58°), is formed, converted by aq. NaOH and reacidification with AcOH into (II), which with hot conc. HCl gives (III). J. W. B.



(*A*.)

Synthesis of 2 : 5-dibenzoylquinol ; 2 : 5-dibenzoylbenzoquinone. R. Pummerer and E. Buchta (Ber., 1936, 69, [*B*], 1018—1021).—Quinol-2 : 5-dicarboxylic acid is converted by Ac_2O containing conc. H_2SO_4 at 100° into the Ac_2 derivative and thence by PCl_5 in boiling C_6H_6 into the corresponding *dichloride*, m.p. 149° after slight softening, which with $AlCl_3$ and C_6H_6 affords 2 : 5-dibenzoylquinol (I), m.p. 199°. (I) is not dehydrogenated by CrO_3 in boiling AcOH, alkaline $K_3Fe(CN)_6$, or PbO_2 in boiling *o*-$C_6H_4Cl_2$ but is transformed by Ag_2O in boiling C_6H_6 into 2 : 5-*dibenzoyl*-p-*benzoquinone* (II), m.p. 228° when placed in bath preheated to 227°. (II) differs entirely from Pechmann's dye. H. W.

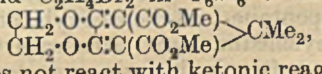
Hydrolysis of 2-hydroxyanthraquinone-β-*d*-glucoside. J. H. Gardner and W. H. Demaree (J. Amer. Chem. Soc., 1936, 58, 757—758).—2-Hydroxyanthraquinone-β-*d*-glucoside ($+H_2O$) (I), m.p. (anhyd.) 244·4—244·7° (corr.), obtained by hydrolysis (method : Robertson, A., 1930, 895) of its Ac_4 derivative, m.p. 170—170·3° (corr.) (prep.: Müller, *ibid.*, 71), is hydrolysed (in suspension under identical conditions) by 0·05*N*-KOH, 0·05*N*-HCl, and approx. 10% borax at 100° with decreasing ease in the order quoted. Hydrolysis occurs less readily than with 1-hydroxyanthraquinone-β-*d*-glucoside and -arabinoside (A., 1935, 983). The rate of hydrolysis of (I) by emulsin at 37° is in accordance with the β-glucoside formulation. H. B.

Additive product of carotene with maleic anhydride. Z. Nakamiya (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 286—287).—Carotene and maleic anhydride give in C_6H_6 an *anhydride*, $C_{40}H_{56},(C_4H_2O_3)_5$, m.p. 285—286°, of which the absorption spectrum shows no remaining double linkings. The corresponding *acid* (*Ba* and *Ag* salts), and a *compound* $C_{40}H_{56},(C_4H_2O_3)Br_{10}$, decomp. 250—260°, are prepared. E. W. W.

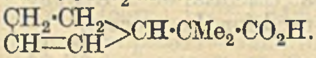
Catalytic reduction of pulegone. B. N. Rutovski, T. A. Kolobelotzkaja, and Z. A. Jaroslavtzeva (J. Appl. Chem. Russ., 1936, 9, 684—689).—Pulegone (I) is converted into menthol (90% yield) by hydrogenation at 180°, in presence of a catalyst prepared by washing 27 : 73 Ni–Al with aq. NaOH for 25—45 min., and then with H_2O, and drying the product in a stream of H_2. Impure (I), from the essential oil of *Ziziphora clinopodioides*, L., may be used for the process. R. T.

Optically active 2-deuterocamphane. E. Bilmann, K. A. Jensen, and E. Knuth (Ber., 1936, 69, [*B*], 1031—1035).—Treatment of *l*-bornyl chloride with Mg and then with H_2O gives a mixture of camphane (I), *l*-camphene, and *d*-dihydrocamphene from which the last-named is removed by distillation; crystallisation of the residue from MeOH–Et_2O affords (I), m.p. 153—154°, $[\alpha]_D$ ±0°. If D_2O is used in place of H_2O, 2-*deuterocamphane* (II), m.p. 153·5—154°, $[\alpha]_D^{20}$ +0·40°±0·05° in Et_2O, is obtained which does not depress the m.p. of (I). Treatment of (II) with H(Pt–C) causes inactivation whereas (I) remains unchanged. H. W.

Pinane group. I. Synthesis of pinononic acid and "ketonopinone" [4 : 6-diketonopinane]. P. C. Guha and K. Ganapathi (Ber., 1936, 69, [*B*], 1185—1194; cf. A., 1935, 975; this vol., 206).—*trans*-Norpinic acid is converted by Ac_2O into *cis*-norpinic anhydride (I) (corresponding *anilic acid*, m.p. 218—219°, and *monoamide*, m.p. 197—198°), (I) and NaOMe in MeOH at 0° afford *Me H* cis-*norpinate*, m.p. 69—71°, converted by the successive action of $SOCl_2$ and NH_2Ph into the corresponding *anilide*, m.p. 174°, and by $SOCl_2$ followed by ZnMeI into *Me_2 pinononate*, b.p. 127°/13 mm. (*semicarbazone*, m.p. 177—178°), hydrolysed to cis-*pinononic acid*, m.p. 129° [*semicarbazone*, m.p. 208° (decomp.); *oxime*, m.p. 175—176°]. The synthesis of 4 : 6-diketonopinane (*loc. cit.*) is described in greater detail. cis-*Norpinyl dichloride*, m.p. about 80° (corresponding *dianilide*, m.p. 269—270°), gives a neutral product with terpene-like odour with MgMeI and a mixture of compounds with ZnMeI. H. W.

Syntheses in the camphane group. I. Attempted synthesis of *apo*camphorquinone. P. G. Guha and S. K. Ranganathan (Ber., 1936, 69, [*B*], 1195—1198).—Condensation of Me_2 diketo*apo*camphorate with Na and $C_2H_4Br_2$ in C_6H_6 or MeOH affords the *substance*  $\begin{matrix}CH_2{\cdot}O{\cdot}C{:}C(CO_2Me)\\CH_2{\cdot}O{\cdot}C{:}C(CO_2Me)\end{matrix}{>}CMe_2$, m.p. 164—165°, which does not react with ketonic reagents or give a coloration with $FeCl_3$. It is hydrolysed by KOH–MeOH to the corresponding dicarboxylic *acid*, m.p. 274—275° (decomp.), and hydrolysed and decarboxylated by boiling dil. H_2SO_4 (1 : 3) to 3 : 4-diketo-1 : 1-dimethyl*cyclo*pentane. The latter substance could not be condensed with $NaNH_2$ and $C_2H_4Br_2$ in Et_2O. H. W.

Camphor series. Structure of camphene-lauronolic acid. O. ASCHAN (Soc. Sci. fenn., Comment. phys.-math., 1935, **8**, No. 1, 13 pp.; Chem. Zentr., 1935, ii, 1555—1556; cf. A., 1916, i, 53).—Distillation of camphenic acid in a stream of CO_2 at atm. pressure affords camphenonic acid and camphene-lauronolic acid (I), $C_9H_{14}O_2$, b.p. 129°/7 mm., $[\alpha]_D$ +2·51° (*Na*, *Ba*, and *Ca* salts; *amide*, m.p. 139°, 142—143°). (I) does not add N_2O_3, is not hydrolysed by 95% HCO_2H at 160—170°, it yields a readily decomposed Br additive product, and, on oxidation ($KMnO_4$), *cyclo*pentanone-3-carboxylic acid and $COMe_2$ are not formed. It is concluded that (I) is



$$\left.\begin{matrix}CH_2\cdot CH_2\\ CH{=}CH\end{matrix}\right>CH\cdot CMe_2\cdot CO_2H.$$

H. N. R.

Optical activity and chemical constitution. Optically active acids and bases. II. MAHAN SINGH and MANOHAR SINGH (J. Indian Chem. Soc., 1935, **12**, 768—770; cf. A., 1935, 1127).—$[\alpha]_D$, $[\alpha]_{5780}$, and $[\alpha]_{5461}$ of p-*diethylaminoanilocamphor* (I), m.p. 102·5°, prepared by heating camphorquinone with *p*-$NH_2\cdot C_6H_4\cdot NEt_2$, EtOH, and anhyd. Na_2SO_4, have been determined in several solvents. (I) and the corresponding Me_2 compound (*loc. cit.*) are both photo- and thermo-tropic. The two forms of these compounds have different $[\alpha]_D$. The changes in $[\alpha]_D$ of the two forms of (I) in EtOH solution indicate an equilibrium. H. G. M.

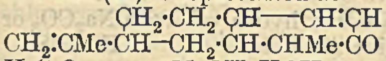
Salts of camphor-10-sulphonic acid (Reychler's acid). S. BERLINGOZZI and R. LENOCI (Boll. Chim. farm., 1936, **75**, 270, 273—276).—*Hexamethylenetetramine*, m.p. 165—166°, $[\alpha]_D^{20}$ +13·2° (in H_2O), *piperazine*, decomp. about 250°, $[\alpha]_D^{20}$, +17·5°, *antipyrine*, m.p. 164°, $[\alpha]_D^{20}$ + 11·9°, and *pyramidone*, m.p. about 180° (decomp.), $[\alpha]_D^{20}$ +10·4°, *camphor*-10-*sulphonates* are prepared. E. W. W.

Camphor series. II. Synthesis of oximinothiocamphor and its application as an indicator in acidimetry and alkalimity. D. C. SEN (J. Indian Chem. Soc., 1935, **12**, 751—755).—Thiocamphor, *iso*amyl nitrite, Et_2O, and $NaNH_2$ give *oximinothiocamphor*, m.p. 148° (*Ni* and *Co* salts), suitable as an indicator in acid- and alkal-imitry. ($p_K=8{\cdot}8$; p_H range 8·6—9·0.) It is a sensitive reagent for Co, detecting 1 part in 50,000 of H_2O.
H. G. M.

Syntheses in the camphane group. II. Synthesis of ketohomonorcamphor [di*cyclo*-[1:2:3]-octane-2 : 4-dione]. P. C. GUHA and S. K. RANGANATHAN (Ber., 1936, **69**, [*B*], 1199—1206).—Mainly an extended account of work already reported (A., 1935, 1245). The following appears new. Acetyl*cyclo*pentane-3-carboxylic acid is oxidised by KOBr to *cis*-*cyclo*pentane-1 : 3-dicarboxylic acid. Condensation of methylenedimalonic ester with $C_2H_4Br_2$ and NaOEt gives, after hydrolysis and decarboxylation of the product, glutaric anhydride. *cis*-*cyclo*Pentane-1 : 3-dicarboxylic anhydride and MgMeI in Et_2O do not appear to yield the ketonic acid. Me_2 *cis*-*cyclo*pentane-1 : 3-dicarboxylate, $Me_2C_2O_4$, and NaOMe give unchanged material and *trans*-*cyclo*pentane-1 : 3-dicarboxylic acid. Et_2 1 : 3-dibromo*cis*-*cyclo*pentane-1 : 3-dicarboxylate and $C_2Na_2(CO_2Et)_4$ do not react in boiling C_6H_6. H. W.

The santene inversion of fenchyl alcohol and its conditions. N. J. TOIVONEN (Suomen Kem., 1936, **9**, **B**, 15—16).—Al salts and other catalysts are divided into those which catalyse the conversion of fenchyl alcohol (I) into 1-methylsantone (II) and into fenchenes, respectively (cf. this vol., 338). The santene inversion seems to be favoured by influences which increase the ionisation of esters of (I), *e.g.*, cresol, β-$C_{10}H_7\cdot OH$. Using $AlPO_4$, α-, β-, γ-, and *cyclo*-fenchene are obtained. Fenchenes are more readily polymerised than (II); polymerising catalysts therefore give terpene mixtures richer in (II). Catalysts which yield (II) also give monocyclic terpenes. *iso*Fenchyl alcohol and kaolin give mainly polymerides, but also (II). *cyclo*Fenchene is very readily polymerised. E. W. W.

α-Cyperone, a sesquiterpene ketone from the oil of *Cyperus rotundus*. A. E. BRADFIELD, B. H. HEGDE, B. S. RAO, J. L. SIMONSEN, and (in part) A. E. GILLAM (J.C.S., 1936, 667—677).—The higher-boiling fractions of the oil, treated with semicarbazide acetate, give *α-cyperonesemicarbazone* (I), m.p. 216°, $[\alpha]_{5461}$ +178° in $CHCl_3$, hydrolysed to *α-cyperone*, $C_{15}H_{22}O$ (II), b.p. 177°/20 mm., $[\alpha]_{5461}$ +138° (*oxime*, m.p. 150·5°, $[\alpha]_{5461}$ +134° in EtOH; 2 : 4-*dinitrophenylhydrazone*, m.p. 209—210°; *nitroguanylhydrazone*, decomp. 203—204°, $[\alpha]_D$ +196°). (II) with Na and amyl formate yields hydroxymethylene-α-cyperone (2 : 4-*dinitrophenylhydrazone*, m.p. 159—160°). Reduction of (II) with Pd–H_2 affords *tetrahydro-α-cyperone* (III), b.p. 151—152°/14 mm., $[\alpha]_{5461}$ +14·8° (*semicarbazone*, decomp. 173—175°; *oxime*, m.p. 116—117·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 151—152°), and with Na–EtOH gives *dihydro-α-cyperol* (IV), b.p. 167—168°/15 mm. $[\alpha]_{5461}$ +17·7° in EtOH (3 : 5-*dinitrobenzoate*, m.p. 157—158°), dehydrogenated (Se) to eudalene. Hydroxymethylenetetrahydro-α-cyperone forms a 2 : 4-*dinitrophenylhydrazone*, m.p. 182—183°. Oxidation of (II) with O_3 gives CH_2O, and a dibasic keto-acid, $C_{13}H_{20}O_5$ (*Me_2* ester, b.p. 190—197°/11 mm., and its *semicarbazone*, decomp. 245—246°), and with H_2O_2–NaOH yields 6-*acetyl*-1-*methyl*-4-iso*propenyl*cyclo*hexane*-1-*carboxylic acid*, m.p. 112°, $[\alpha]_{5461}$ +62·6° in MeOH (*semicarbazone*, decomp. 180—181°; *phenylsemicarbazone*, decomp. 200°). Ozonisation of (I) leads to a *semicarbazone*, decomp. 185—187°. (IV) is ozonised to a neutral oil, which is oxidised (H_2CrO_4) to a diketone (*dioxime*, decomp. 258—259°; *disemicarbazone*, decomp. 251—252°) (using an impure specimen containing α-cyperol, a substance forming a *di*- or *tri-phenylsemicarbazone*, decomp. 222—223°, has been obtained). Ozonolysis of dihydro-α-cyperyl 3 : 5-dinitrobenzoate gives CH_2O and a *ketone*, $C_{21}H_{26}O_7N_2$, m.p. 148—149°, from which CHI_3 is derived by oxidation with Fuson's reagent. (III) and MgMeI afford a mixture, which is dehydrogenated (Se) to 1 : 2-*dimethyl*-7-iso*propylnaphthalene* (V), b.p. 149—151°/9 mm. (*picrate*, m.p. 92—93°; *s*-$C_6H_3(NO_2)_3$ *derivative*, m.p. 107—109°). Reduction of hydroxymethylene-α-cyperone with Pd–H_2 followed by Na–EtOH leads to an oil, dehydrogenated (Se) to a hydrocarbon, $C_{15}H_{18}$ (*picrate*, m.p. 102·5—104°; *s*-$C_6H_3(NO_2)_3$ *derivative*, m.p. 116—118°). (I) with NaOEt affords α-*cyperene*, b.p. 132—133°/15 mm., which could not be reduced by Na. (III) is 1 : 10-dimethyl-7-*iso*propyldecal-2-one and (II) is represented as

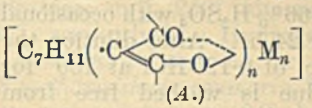


$$\begin{array}{l}\qquad\;\;\;CH_2{\cdot}CH_2{\cdot}CH\text{——}CH{:}CH\\ CH_2{:}CMe{\cdot}CH\text{–}CH_2{\cdot}CH{\cdot}CHMe{\cdot}CO\end{array}$$

(II) is isomerised by $H_2C_2O_4$,aq. or MeOH–KOH to β-*cyperone*, b.p. 175—176°/16 mm. $[\alpha]_{5461}$ +239° (*semicarbazone*, decomp. 207°; *oxime*, m.p. 138°, $[\alpha]_{5461}$ +217° in EtOH; 2 : 4-*dinitrophenylhydrazone*, decomp. 218—219°; *nitroguanylhydrazone*, m.p. 197°, $[\alpha]_D$ +220° in $CHCl_3$), which must differ only stereochemically from (II). *Homocuminyl alcohol*, b.p. 129°/10 mm. (p-*xenylcarbamate*, m.p. 144—145°), obtained from the corresponding Et ester, is converted into the *bromide*, b.p. 136°/14 mm., which with Et methylpotassiomalonate forms *Et homocuminylmethylmalonate*, b.p. 200°/13 mm. The ester with H_2SO_4 yields 2-*methyl*-7-iso*propyl*-1 : 2 : 3 : 4-*tetral*-1-*one*, b.p. 155—160°/12 mm. (*phenylsemicarbazone*, m.p. 180—181°; 2 : 4-*dinitrophenylhydrazone*, m.p. 177—178°), which with MgMeI forms an oil, dehydrogenated (Se) to (V). Tetrahydroeremophilone and MgMeI give a substance, dehydrogenated (Se) to 1 : 3 : 7-$C_{10}H_5Me_2Pr^{\beta}$ (*picrate*, m.p. 113—114·5°; *s*-$C_6H_3(NO_2)_3$ *derivative*, m.p. 141—142°).

o-*Methylbenzyl* Pr^{β} *ketone*, b.p. 125—126° (*semicarbazone*, m.p. 128—129°; *phenylsemicarbazone*, m.p. 183°), with $CHMeBr{\cdot}CO_2Et$ and Zn affords *Et γ*-o-*tolyl-α-methyl*-β-iso*propylbutyrate*, b.p. 165°/13 mm., which with H_2SO_4 gives 2 : 5-*dimethyl*-3-iso*propyl*-1 : 2 : 3 : 4-*tetral*-1-*one*, b.p. 185—190°/22 mm. (*phenylsemicarbazone*, m.p. 222—223°). The ketone is reduced and dehydrogenated to 1 : 6-dimethyl-7-*iso*propylnaphthalene, b.p. 154—158°/13 mm. (*picrate*, m.p. 124—126°; *styphnate*, m.p. 141—142°). *Et homocuminylmalonate*, b.p. 198°/13 mm., is converted with H_2SO_4 into 7-*iso*propyl-1 : 2 : 3 : 4-tetral-1-one, b.p. 158—160°/17 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 223—224°), which with MgEtI followed by dehydrogenation affords 1 : 7-$C_{10}H_6EtPr^{\beta}$ (*picrate*, m.p. 65—67°; *s*-$C_6H_3(NO_2)_3$ derivative, m.p. 79—81°). The absorption spectrum of (II) indicates an αβ-unsaturated ketone. F. R. S.

Colouring matter in the wood of "Hinoki" tree. I. Hinokitin and hinokitiol. T. Hozoe (Bull. Chem. Soc. Japan, 1936, **11**, 295—298).—Discrepancies in earlier work by Hirao (J. Chem. Soc. Japan, 1926, **47**, 666, 743) and Tsuchihashi *et al.* (Rep. Gov. Res. Inst. Formosa, 1920, 1) are investigated. From the ethereal oil of the wood of the "Hinoki" tree (*Chamæcyparis obtusa*, Lieb. and Zucc.) are isolated *l*-rhodinic acid, $C_{10}H_{18}O_2$, and a phenolic substance *hinokitiol*, $C_{10}H_{12(14)}O_2$ (I) (no OMe; gives liquid products with CO reagents), converted by $FeCl_3$ into *hinokitin*, $C_{30}H_{33}O_6Fe$, m.p. 251° (absorption max. 584, 540 mμ) (II) (*A*; M=Fe, *n*=3), an Fe complex salt of (I). The interconversion 3(I)+FeX_3 $\rightleftharpoons$ (II)+3HX is realised. (I) also forms complex *salts* (all of type *A*) with $Cr^{\cdot\cdot\cdot}$, m.p. 230°, $Co^{\cdot\cdot\cdot}$, m.p. 208°, $Cu^{\cdot\cdot}$, m.p. 177°, $Ni^{\cdot\cdot}$, m.p. 242°, $Co^{\cdot\cdot}$, m.p. 210°, $Mn^{\cdot\cdot}$, m.p. > 300°, $Cd^{\cdot\cdot}$, m.p. > 300°, $Zn^{\cdot\cdot}$, and $Mg^{\cdot\cdot}$, m.p. > 300°; those with bivalent metals form cryst. compounds with 2 mols. of org. bases. By catalytic reduction (I) absorbs 3—4 H_2, and the product no longer forms complex salts. J. W. B.



(*A*.)

Limonin, the bitter principle of orange kernels. G. Koller and H. Czerny [with K. Locker and W. Maas] (Monatsh., 1936, **67**, 248—268).—The air-dried material is extracted successively with light petroleum and EtOH. The syrupy residue is treated with H_2O and much Et_2O, which induces crystallisation of a mixture of bitter principles. Limonin (I) is isolated therefrom by dissolution in dil. NaOH or KOH, acidification of the solution at 0°, and suspension of the pptd. OH-acids in EtOH, when (I) slowly crystallises. Alternatively the mixture is treated with Ac_2O in C_5H_5N, whereby (I) remains unchanged whereas iso*limonin* (II) is transformed into a more freely sol. Ac derivative. (II) is best isolated by regulated extraction of the mixture with boiling C_6H_6, which removes more freely sol. (I). (I), m.p. 280° (vac.; decomp.), is probably $C_{23}H_{26}O_7$. The presence of :CO could not be established. Under drastic conditions acetylation occurs to only a slight extent. With cold MgMeI little CH_4 is evolved, but in boiling solution the vol. of gas is equiv. to about 1 OH. One lactone group is certainly, a second probably present. Catalytic hydrogenation (Pd–C) of (I) in abs. EtOH leads to absorption of 3 H_2 and production of an amorphous product which passes on contact with H_2O into the cryst. *hexahydrolimonic acid* (III), $C_{23}H_{34}O_8$, decomp. 175—178° (vac.). When kept over P_2O_5 at 140°/vac. (III) loses H_2O with apparent formation of polymerised material. It is unchanged by $CaCl_2$ in C_6H_6. Ac_2O transforms it into a non-cryst. *Ac* derivative from which it is regenerated by EtOH–H_2O. Its non-cryst. *Me* ester appears to be $C_{24}H_{34}O_7$. During hydrogenation small amounts of *tetrahydrolimonin*, $C_{23}H_{30}O_7$, m.p. 282° (vac.), appear to be produced. Treatment of (I) with molten KOH affords partly hydrogenated alkylnaphthalenes from which by treatment with Se at 300° 1 : 2 : 5-$C_{10}H_5Me_3$ and possibly a $C_{10}H_6Me_2$ are isolated; the acidic products contain *m*-$C_6H_4(CO_2H)_2$. Oxidation of (I) with $KMnO_4$, HNO_3, or H_2O_2 gives ill-defined products whereas MnO_2 and boiling 57% H_2SO_4 give $C_6H(CO_2H)_5$. (II), probably $C_{23}H_{28}O_7$, m.p. 264° (vac.; decomp.), contains 2 OH (Zerevitinov) and appears to give a *diacetate*. H. W.

Capsanthol, a reduction product of capsanthin. P. Karrer and H. Hübner (Helv. Chim. Acta, 1936, **19**, 474—479).—Capsanthin (I) and $Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$–C_6H_6 gives *capsanthol* (II), $C_{40}H_{57}(OH)_3$, m.p. 175—176° (photomicrograph), isolated by adsorption on CaO. (II) absorbs 10 H_2 on micro-hydrogenation and its adsorption spectrum (max. at 5080 and 4770 A. in CS_2) closely resembles that of (I), confirming the presence of a CO in (I) at the end of a series of 10 ethylenic linkings. R. S. C.

Formation of lignin in wood. P. Klason (Ber., 1936, 69, [*B*], 676—678).—For the determination of lignin in wood the finely-divided sample is extracted with Et_2O and dried at 100°. 1—1·3 g. is kept in contact with 50 c.c. of 65—66% H_2SO_4 with occasional shaking at room temp. for 24 hr. After dilution the ppt. is heated with 50 c.c. of 0·1*N*-HCl at 100° for about 12 hr. The residue is washed free from mineral acid, dried at 75° and then at 100°, weighed, and incinerated. The possible formation of lignin in plants from CO_2 and H_2O through CH_2O is discussed. The part played by H_3PO_4 is considered. The "lignin fermentation" appears invariably associated with the production of pentoses. H. W.

Dioxan-lignin and the pigment of ebony wood. R. S. Hilpert and S. Wisselinck (Ber., 1936, 69, [*B*], 680—684).—Xylose is transformed by HCl–dioxan into a pitch-like mass converted by H_2O into a black powder. Under like conditions, fructose gives a brown solution from which H_2O ppts. a similar material. Glucose does not become discoloured but its chemical properties are altered. In composition, which varies somewhat with the [HCl] used, the solid products are closely allied to the lignins, from which they differ mainly in the absence of OMe. The assumption that HCl–dioxan simply removes lignin and incrustations from wood and leaves cellulose is of doubtful validity. Wedekind's method (this vol. 207) for the isolation of the pigment of ebony wood is criticised. H. W.

Further resinol from matai (*Podocarpus spicatus*). L. H. Briggs and D. A. Peak (J.C.S., 1936, 724).—From the mother-liquors of matairesinol, conidendrin, m.p. 254—255°, has been isolated (cf. Haworth *et al.*, this vol., 80). F. R. S.

Pigments of *Lactarius deliciosus*, L. II. H. Willstaedt (Ber., 1936, 69, [*B*], 997—1001; cf. A., 1935, 495).—The material is extracted with EtOH and then with $COMe_2$. The $COMe_2$ extract is treated with H_2O and light petroleum. The latter extract is chromatographed with Al_2O_3 thus giving *lactarazulene* (I), b.p. 155—160°/2·5—3 mm. [additive *compound*, $C_{21}H_{21}O_6N_3$, m.p. 122—123°, with 1 : 3 : 5-$C_6H_3(NO_2)_2$]. (I) is closely similar to but not identical with the azulene from camomile oil. Both sources contain a second azulene and also a green product. H. W.

Red gossypol.—See this vol., 912.

Catalytic transformations of heterocyclic compounds. II. Conversion of 2-methylfuran into 2-methylpyrrole and 2-methylthiophen. III. Reciprocal transformations of the simplest five-membered heterocyclic compounds. J. K. Juriev (Ber., 1936, 69, [*B*], 1002—1004; cf. this vol., 481).—2-Methylfuran gives 2-methylpyrrole when passed with NH_3 over Al_2O_3 at 450° and 2-methylthiophen when passed with H_2S over the catalyst at 350°. The conversion of furan (I) into pyrrole (II) and thiophen (III) takes place with good yields, but yields are poor in the changes (II) → (III), (III) → (II), (II) → (I), and (III) → (I). H. W.

Resolution of α-furylmethylcarbinol. D. I. Duveen and J. Kenyon (J.C.S., 1936, 621—623).—*dl*-α-Furylmethylcarbinol (p-*xenylurethane*, m.p. 114°; *acetate*, b.p. 177°/760 mm.) with *o*-$C_6H_4(CO)_2O$ gives dl-α-*furylmethylcarbinyl H phthalate*, m.p. 80°, which is resolved through the *quinidine* salts, m.p. 81°, $[\alpha]^{19}_{5893}$ +76·8°, and $[\alpha]^{20}_{5893}$ +13·4° in $CHCl_3$, into *d*- and *l*-α-furylmethylcarbinyl H phthalate, m.p. 61°, $[\alpha]^{19}_{5893}$ +39·6° and −39·3° in $CHCl_3$. *d*- and *l*-Furylmethylcarbinol have b.p. 70°/15 mm., α^{19}_{5893} +10·29° and −40·07°, and are obtained by hydrolysis of the H phthalates with NaOH; hydrolysis with Na_2CO_3 or steam leads to inactive alcohols. F. R. S.

Condensation of acetone and mesityl oxide with furfuraldehyde. P. P. Surmin (J. Gen. Chem. Russ., 1935, 5, 1642—1644).—$COMe_2$ and furfuraldehyde (I) in presence of 3% of NaOH at 0° yield mono- and di-furfurylideneacetone (*phenylhydrazones*, m.p. respectively 123° and 121—122°). Mesityl oxide and (I) in presence of 50% of NaOH afford *furfurylidenemesityl oxide*, m.p. 140—145°, not yielding a phenylhydrazone. R. T.

Identity of *iso*psoralene, a component of the seeds of *Psoralea corylifolia*, L., with angelicin from the roots of *Angelica Archangelica*, L. H. S. Jois and B. L. Manjunath (Ber., 1936, 69, [*B*], 964—967).—The solid which crystallises from the oil from the seeds of *P. corylifolia*, L., is separated by EtOH into psoralene and iso*psoralene* (I), m.p. 142°, identical with angelicin (Späth, A., 1934, 779, 899). (I) is oxidised by alkaline H_2O_2 to furan-2 : 3-dicarboxylic acid. Reduction of (I) by Na–Hg in alkaline solution affords 3-*hydroxy*-4-β-*carboxyethylcoumarone* (II), m.p. 124·5°, which passes at 155°/vac. into the corresponding *lactone*, m.p. 74·5°. Methylation (Me_2SO_4) and subsequent hydrolysis of (I) gives 3-*methoxy*-4-β-*carboxyvinylcoumarone* (III), m.p. 142—144°, converted into an *isomeride*, m.p. 214°, by repeated sublimation in high vac., and reduced to the corresponding saturated *acid*, m.p. 77°, also obtained by methylation of (II). Oxidation of (III) by $KMnO_4$ yields an *acid*, $C_9H_8O_4$, m.p. 107°. H. W.

6-Methylcoumarin and its methylation products. K. Chang and P. P. T. Sah (J. Chinese Chem. Soc., 1936, 4, 84—88).—5-Methylsalicylaldehyde with anhyd. NaOAc and Ac_2O containing some I at 180—190° affords 6-methylcoumarin, m.p. 76·5—77·5° (lit., 74·5°), which with MeI in EtOH–NaOEt at room temp. affords Me *cis*-5-methyl-*o*-methoxycinnamate (cf. A., 1908, i, 441), whereas with NaOH–Me_2SO_4, the *trans*-isomeride (cf. A., 1911, i, 295) is formed. J. L. D.

Relation between odour and constitution of alkoxycoumarins. New product with a celery odour. A. S. Pfau (Riechstoffind., 1935, 10, 57—58; Chem. Zentr., 1935, ii, 1457).—The odours of the following are described: 6-methoxy- (odourless), 6-, m.p. 106—107°, and 7-*ethoxy-coumarin*, m.p. 89°; 6-*methoxy*-, m.p. 163—164°, 6-*ethoxy*-, m.p. 113—114°, 7-methoxy-, 7-*ethoxy*-, m.p. 114·5° (strong celery odour), 7-n-*propoxy*-, m.p. 72—73°, 7-iso*butoxy*-, m.p. 55—56°, and 7-*allyloxy*-, m.p. 103° (odourless), -4-*methylcoumarin*; 7-*ethoxy*-4-*methyldihydrocoumarin*, m.p. 30°. H. N. R.

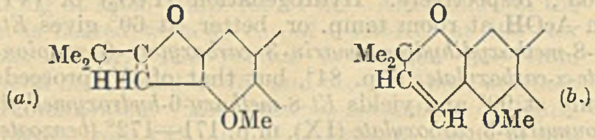
Synthesis of coumarins from phenols and β-ketonic esters. V. Constitution of chlororesorcinol and chlororesorcylaldehyde. D. Chak-

RAVARTI and B. GHOSH (J. Indian Chem. Soc., 1935, **12**, 791—797).—The diazo-anhydride of 8-amino-7-hydroxy-4-methylcoumarin is converted (Sandmeyer) into 8-*chloro*-7-*hydroxy*-4-*methylcoumarin*, m.p. 267° (*Ac* derivative, m.p. 188—189°), which is different from the condensation product of $CH_2Ac{\cdot}CO_2Et$ and 4-chlororesorcinol (I), (cf. A., 1935, 1503). Nitration of 7-hydroxy-3 : 4-dimethylcoumarin gives the 8-NO_2-derivative (*loc. cit.*), reduced by $SnCl_2$–HCl–EtOH to the corresponding 8-NH_2-derivative, m.p. 272°. This is converted into the corresponding *diazo-anhydride*, m.p. 172°, and then (Sandmeyer) into 8-*chloro*-7-*hydroxy*-3 : 4-*dimethylcoumarin*, m.p. 272°, which is different from the condensation product of (I) and $CHMeAc{\cdot}CO_2Et$ (cf. *loc. cit.*). These comparisons confirm the constitution of (I) (cf. A., 1933, 270). Nitration of umbelliferone yields its 6-, m.p. 220° (*Ac* derivative, m.p. 180°), and 8-, m.p. 245° (*Ac* derivative, m.p. 185°) -NO_2-derivatives (cf. J.C.S., 1910, **97**, 1400). The constitution of the latter is confirmed by reduction to 8-*amino*-7-*hydroxycoumarin*, converted (Sandmeyer) into 8-*chloro*-7-*hydroxycoumarin*, m.p. 263°, which is different from the condensation product (II) of (I) and malic acid (*loc. cit.*). (I) with anhyd. $Zn(CN)_2$ and dry HCl in Et_2O gives 5-chlororesorcylaldehyde (III), which with NaOH–$ClCO_2Me$ gives *chlorodicarbomethoxyresorcylaldehyde*, m.p. 58°, this with $CH_2(CO_2H)_2$–AcOH yields *chlorocarbomethoxy*-7-*hydroxycoumarincarboxylic acid* and a trace of 2 : 4-dicarbomethoxycinnamic acid (cf. A., 1934, 775). The former when boiled with Na_2CO_3 gives 6-*chloro*-7-*hydroxycoumarin*-3-*carboxylic acid*, m.p. 284°, decomposed by heat into 6-chloro-7-hydroxycoumarin, identical with (II). H. G. M.

[Attempted] synthesis of furocoumarins from 4-hydroxy-5-methoxy*iso*phthaldialdehyde. K. W. MERZ and J. HOTZEL (Arch. Pharm., 1936, **274**, 292—310).—Attempts to prepare xanthotoxin or an isomeride thereof failed. Guaiacol-4 : 6-dialdehyde (I) with Ac_2O–C_5H_5N gives the *Ac* derivative, m.p. 145—146°, and with P_2O_5–Ac_2O at 100° gives *acetylguaiacol*-4 : 6-*dialdehyde tetra-acetate*, m.p. 136·5°. With NH_2OH these give the dioxime of (I), which with Ac_2O–C_5H_5N gives *acetylguaiacol*-4 : 6-*dialdoxime diacetate* (II), m.p. 148—149°, but with hot Ac_2O yields *acetylguaiacol*-4 : 6-*dinitrile*, m.p. 143°. 4-Aldehydoacetylguaiacol-6-aldoxime with Ac_2O–C_5H_5N gives the *acetate* (III), m.p. 134—135°, and with hot Ac_2O affords 4-*aldehydoacetylguaiacol*-6-*nitrile*, m.p. 117°. Attempts to hydrolyse the nitriles gave resins. (I) with NH_3–EtOH or NH_2Ph–EtOH yields 4-*aldehydoguaiacol*-6-*aldimine*, m.p. 211°, or -6-*aldphenylimine* (IV), m.p. 132°, respectively, and attempts to induce both CHO to react failed. (IV) with Ac_2O–C_5H_5N gives the Ac_3 derivative, m.p. 170°, hydrolysed by aq. EtOH. Attempts to nitrate (I) failed; fuming HNO_3 in EtOH gives 4 : 6-dinitroguaiacol, m.p. 121—122°. (I), piperidine, and $CH_2(CO_2Et)_2$ give a mixture, m.p. 189°, of nitrogenous substances, which with hot AcOH yields *Et* 6-*aldehydo*-8-*methoxycoumarin*-3-*carboxylate* (V), m.p. 209—210° (*phenylhydrazone*, m.p. 215°), and a little Et_3 8-*methoxycoumarin*-3-*carboxylate*-6-*methylenemalonate* (VI), m.p. 148—149°. Hydrolysis of (V) and (VI) by 5% NaOH gives the corresponding *acids* (VII), m.p. 243° (decomp.) [*phenylhydrazone*, m.p. 250° (decomp.)], and (VIII), m.p. 265°, respectively. Hydrogenation (PtO_2) of (VI) in AcOH at room temp. or, better, at 60° gives Et_3 β-8-*methoxydihydrocoumarin*-3-*carboxylate*-6-*propionate*-α-*carboxylate*, m.p. 84°, but that of (V) proceeds only at 90° and yields *Et* 8-*methoxy*-6-*hydroxymethylcoumarin*-3-*carboxylate* (IX), m.p. 171—172° (*benzoate*, m.p. 155°). (V), Ac_2O, and P_2O_5 at 100° afford the *diacetate*, m.p. 127—129°, hydrogenation (PtO_2) of which in AcOH gives the *Ac* derivative, m.p. 139°, of (IX). (VI), H_2SO_4, and KNO_3 at $\ngtr -5°$ give a poor yield of 5- or 7-NO_2-derivative, m.p. 152—154°, which could not be hydrolysed to the acid and gave amorphous products when hydrogenated; the NO_2-acid could also not be obtained directly from (VIII). Similar nitration of (V) affords the 5- and 7-NO_2-*esters*, m.p. 185—186° [*phenylhydrazone*, m.p. 256° (decomp.)] and 124° [*phenylhydrazone*, m.p. 227·5° (decomp.)], respectively, or vice versa, which decompose when hydrolysed, but with H_2–Pt or H_2–Pd–$BaSO_4$ in AcOH absorb 2 H_2 to yield *benzisooxazoles*, m.p. 208—210° and 246° (decomp.), respectively, both resistant to further reduction. (VII) with 65% HNO_3 in conc. H_2SO_4 at 0° gives the 5- and 7-NO_2-*acids*, m.p. 145° [*phenylhydrazone*, m.p. 236° (decomp.)] and 178° [*phenylhydrazone*, m.p. 269° (decomp.)], respectively, or vice versa. The NO_2-esters with Ac_2O–P_2O_5 afford the *diacetates*, m.p. 197° and 131—132°, respectively, which are hydrogenated (Pd or PtO_2) in AcOH to *Et* 5- and 7-*hydroxylamino*-8-*methoxy*-6-*acetoxymethylcoumarin*-3-*carboxylate*, m.p. 164—165° and 116°, respectively, or vice versa. Attempts to decarboxylate (VII) failed. R. S. C.

Constituents of the bark of *Zanthoxylum Americanum* (Mill). I. Xanthoxyletin. (MISS) J. C. BELL, A. ROBERTSON, and T. S. SUBRAMANIAM (J.C.S., 1936, 627—633).—Xanthoxyletin, $C_{14}H_{11}O_3{\cdot}OMe$ (I), m.p. 133°, has been isolated and is the same compound as xanthoxylin *N* (cf. Gordin, A., 1907, i, 68). (I) is hydrolysed (NaOH) to phloroglucinol Me ether (*di-p-nitrobenzoate*, m.p. 199—200°) and $COMe_2$, and oxidation with $KMnO_4$–NaOH leads to α-hydroxy*iso*butyric acid. With NaOH–Me_2SO_4, (I) is converted into O-*methylxanthoxyletinic acid* (II), m.p. 179·9—180·5° (*Me* ester, m.p. 78·5—79·5°), an unsaturated acid. Hydrogenation (Pd–H_2) of (I) gives *dihydroxanthoxyletin*, m.p. 144·5—145·5°, which with NaOH–Me_2SO_4 forms O-*methyldihydroxanthoxyletinic acid*, m.p. 171—172°, reduced to the -*tetrahydro-acid*, m.p. 150·5—151·5°, also obtained from (II). Ozonisation of (I) affords apo*xanthoxyletin*, m.p. 217—218° [*phenylhydrazone*, m.p. 251° (decomp.); Ac_3 derivative, m.p. 151—152°], reduced (Pd–H_2) to *deoxy*apo*xanthoxyletin* (III), m.p. 197—198°, the *Me ether*, m.p. 138—139°, of which with Me_2SO_4 gives 2 : 4 : 6-*trimethoxy*-3-*methylcinnamic acid* (IV), m.p. 163—164°, reduced (Pd–H_2) to 2 : 4 : 6-*trimethoxy*-3-*methyldihydrocinnamic acid*, m.p. 139—140°. 2-Hydroxy-4 : 6-dimethoxy-3-methylbenzaldehyde, $CN{\cdot}CH_2{\cdot}CO_2H$, and NaOH yield 4 : 6-dimethoxy-3-methylsalicylidenecyanoacetic acid, hydrolysed and cyclised to 5 : 7-dimethoxy-8-methylcoumarin-3-carboxylic acid, which is decarboxylated to 5 : 7-

dimethoxy-8-methylcoumarin, m.p. 187—188°. Hydrolysis and methylation of this coumarin give (IV).



(I.)

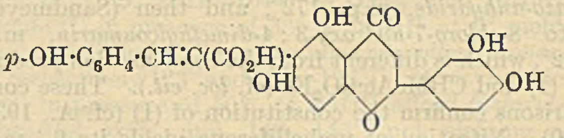
Hence (III) must be either 7-hydroxy-5-methoxy- or 5-hydroxy-7-methoxy-6-methylcoumarin and (I) has the structure of type (*a*) or (*b*). F. R. S.

Natural coumarins. XVI. Coumarins of the root of *Heracleum sphondylium*. L. E. Späth and A. F. J. Simon (Monatsh., 1936, 67, 344—351).—The dried material is extracted with Et_2O and the extract is washed with dil. alkali. The neutral portion remaining in the Et_2O is hydrolysed, the unsaponifiable matter is removed, and ring-closure of the lactones is effected by addition of acid. The lactone mixture is separated into its components by fractional distillation in high vac. combined with suitable crystallisation. Thus are isolated *iso*pimpinellin, m.p. 147—149°, pimpinellin, m.p. 117—119°, *iso*bergapten, m.p. 217—219°, *sphondylin* (I), $C_{12}H_8O_4$, m.p. 161—163°, and *sphondin* (II), $C_{12}H_8O_4$, m.p. 189—191°. (I) and (II) contain 1 OMe and are isomeric with bergapten; when oxidised with H_2O_2 they give furan-2 : 3-dicarboxylic acid. H. W.

Antiseptics and anthelmintics. II. Synthesis of 7-hydroxy-6-benzyl- and -6-*n*-hexyl-flavone. D. R. Dhingra, H. L. Uppal, and K. Venkataraman (Proc. Indian Acad. Sci., 1936, 3, A, 206—210).—2 : 4-Dihydroxydiphenylmethane (Klarmann, A., 1926, 515) is converted (Hoesch) into 5-*benzylresacetophenone* (I), m.p. 153° (*dinitrophenylhydrazone*, m.p. 221°), benzylated to the 4-O·CH_2Ph *derivative*, m.p. 111°, converted by PhCHO–50% NaOH into 2-*hydroxy*-4-*benzyloxy*-5-*benzylchalkone*, oxidised (SeO_2–C_5H_{11}·OH at 150°) to 7-*benzyloxy*-6-*benzylflavone*, m.p. 222°, debenzylated by HBr–AcOH to 7-*hydroxy*-6-*benzylflavone*, m.p. 267° (*Ac* derivative, m.p. 191°), also obtained together with its 3-*Bz* derivative, m.p. 229°, from (I) and Bz_2O–NaOBz and subsequent hydrolysis with 10% KOH–EtOH. By similar reactions from α-2 : 4-dihydroxyphenyl-*n*-hexane are obtained 5-n-*hexylresacetophenone*, m.p. 85°, b.p. 195—200°/3—4 mm. (*dinitrophenylhydrazone*, m.p. 183—184°); 2-*hydroxy*-4-*benzyloxy*-5-n-*hexylacetophenone*, m.p. 94°; 2-*hydroxy*-4-*benzyloxy*-5-n-*hexylchalkone*, m.p. 92°; 7-*benzyloxy*-, m.p. 120°, and 7-*hydroxy*-6-n-*hexylflavone*, m.p. 191—192° (*Ac* derivative, m.p. 104°). J. W. B.

Constitution of oroxylin-*A*, a yellow colouring matter from the root-bark of *Oroxylum indicum*, Vent. R. C. Shah, C. R. Mehta, and T. S. Wheeler (J.C.S., 1936, 591—593).—Oroxylin-*A* (probably identical with oroxylin; cf. Naylor and Dyer, J.C.S., 1901, 79, 954) has been isolated in 0·86% yield, and from its reactions appears to be 6-*O*-methylbaicalein (5 : 7-dihydroxy-6-methoxyflavone). It forms 5 : 7-*diacetoxy*-, m.p. 131—132°, and 5-*hydroxy*-7-*benzoyloxy*-6-*methoxyflavone*, m.p. 211°; hydrolysis with KOH gives BzOH and demethylation gives baicalein. Monomethyloroxylin-*A* corresponds in properties with 5-hydroxy-6 : 7-dimethoxyflavone [*platinichloride*, m.p. 185—187° (decomp.); 5-*Ac* derivative, m.p. 130—131°; 5-*Bz* derivative, m.p. 206—207°]. F. R. S.

Fukugenetin, a rearrangement product of fukugetin. M. Murakami and T. Irie (Bull. Chem. Soc. Japan, 1936, 11, 288—292).—Fukugetin and hot 30% aq. KOH in H_2 give a mixture (I) of fukugetin (II) and *isofukugetin* (III), m.p. > 380°, which are *cis-trans* isomerides with the formula shown. (II) and



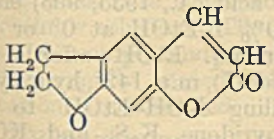
(III) cannot be separated directly from (I), but methylation gives the *Me_6 ethers*, m.p. 204—206°, and (IV), m.p. 199—200°, of (II) and (III), respectively, separable by fractionation from EtOH; (IV) shows only 5 OMe by a Zeisel determination, but a sixth under the conditions used for NMe and is obtained from the *Me_5 ether* (V) described below by further methylation. Further, (I) and H_2SO_4–EtOH give (II), which is unaffected, and *anhydroisofukugetin* (VI), $C_{24}H_{14}O_8$, m.p. > 380°, also obtained from pure (III); the Ac_3 derivative, m.p. 267°, is obtained from (VI) or from (I) by hot Ac_2O–NaOAc, and, since (II) is isomerised to (III) by this reagent, the yield from (I) is excellent. Hydrolysis of (VI) by 10% KOH at room temp. gives (III). Methylation of (VI) gives (V), m.p. 178·5—179° (1 active H); (IV) and 10% KOH give an *acid*, $C_{28}H_{24}O_9$, m.p. 258—260°, which proves the presence of CO_2H in (II) and (III). The loss of one active H (Ac_3 derivative only) in the formation of (VI) is noted. R. S. C.

Chromone group. XIX. Synthesis of genkwanin. H. S. Mahal and K. Venkataraman (J.C.S., 1936, 569—570).—Condensation of 2 : 4 : 6-trimethoxyacetophenone and *p*-CH_2Ph·O·C_6H_4·CO_2Me with Na at 120° affords ω-4′-*benzyloxybenzoyl*-2 : 4 : 6-*trimethoxyacetophenone*, m.p. 101—102°, which with $AlCl_3$–$PhNO_2$ gives only a poor yield of (I) (below). 2-Hydroxy-4 : 6-dimethoxyacetophenone with *p*-CH_2Ph·O·C_6H_4·CHO and NaOH–EtOH affords 2-*hydroxy*-4′-*benzyloxy*-4 : 6-*dimethoxychalkone*, m.p. 159°, oxidised by SeO_2 in boiling C_5H_{11}·OH to 4′-*benzyloxy*-5 : 7-*dimethoxyflavone* (I), m.p. 178°, converted by HCl–AcOH into *genkwanin* 5-*Me ether*, m.p. 298° (*Ac* derivative, m.p. 220°), partly demethylated by $AlCl_3$–$PhNO_2$ to genkwanin (5 : 4′-dihydroxy-7-methoxyflavone) identical with the natural product (cf. Tseng, J. Pharm. Soc. Japan, 1935, No. 636, 30). J. W. B.

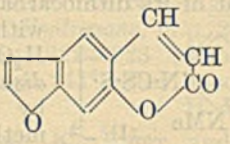
Constitution of awobanin and awobanol, the colouring matter of awobana and its co-pigment. (Miss) C. Kuroda (Bull. Chem. Soc. Japan, 1936, 11, 265—271).—Details are given for the isolation of awobanin chloride (I), $+5H_2O$, and picrate, $+5H_2O$ (cf. A., 1935, 1290), its decomp. by cold NaOH to give *p*-coumaric acid (II), its hydrolysis by cold 20% aq. HCl to glucose and awobanin-*A* (III) chloride, $+3H_2O$, and by hot acid to delphinidin chloride, and its fusion with NaOH to gallic acid and phloroglucinol. (III) is shown to be delphinidin-3 : 5-diglucoside and (I) a compound of this glucoside and (II). A co-pigment, *awobanol*, isolated as *chloride*, m.p. 216° (*Ac* derivative, m.p. 148—156°), is obtained, which on NaOH fusion gives p-$C_6H_4Ac{\cdot}OH$ and p-$OH{\cdot}C_6H_4{\cdot}CO_2H$. R. S. C.

Constitution of natural colouring matters, kuromanin, shisonin, and nasunin. (Miss) C. Kuroda and M. Wada (Bull. Chem. Soc. Japan, 1936, **11**, 272—287).—Details are given of the isolation of kuromanin from the H_2O-sol. and -insol. portions of "kuromane" from 4 sources and of the proof of its identity with chrysanthemin (cf. A., 1935, 1040). Details are given of the isolation from the leaves of "shiso" (cf. A., 1935, 674) of *shisonin*-A (I) and -B (II); (I) is proved to be a cyanin and (II) a compound thereof with p-coumaric acid (III). "Nasu," the fruit of *Solanum melongena*, L., var. *esculentum*, Ness, yields to MeOH–HCl *nasunin chloride* (IV), $+10H_2O$ (*picrate*, $+4H_2O$), purified by $Pb(OAc)_2$ etc., which with cold aq. HCl gives *nasunin*-A *chloride* (V), decomp. 197°, and yields delphinidin chloride; these pigments are probably not identical with the awobana pigments. Probably (V) is delphinidin-3-disaccharide and (IV) contains (III) attached to the sugar nucleus. R. S. C.

Synthesis and constitution of psoralene. E. Späth, B. L. Manjunath, M. Pailer, and H. S. Jois (Ber., 1936, **69**, [*B*], 1087—1090).—6-Hydroxycoumarone is hydrogenated (Pd–C in AcOH) to 6-hydroxycoumarone, m.p. 61°, which is condensed with malic acid and conc. H_2SO_4 at 120° to *dihydropsoralene*



(I.)

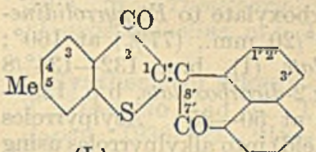


(II).

(I), m.p. 204°. Dehydrogenation of (I) with Pd-sponge at 170° gives psoralene (II), m.p. 171°, identical with the natural substance. Methylation, oxidation, and renewed methylation of (II) gives Me_2 2 : 4-dimethoxybenzene-1 : 5-dicarboxylate, m.p. 147—148°, thus confirming the assigned structure. H. W.

Partial oxidation of metathioxen. I. J. Rinkes (Rec. trav. chim., 1935, **54**, 940—942).—The conclusion of Steinkopf *et al.* (A., 1935, 354) that partial oxidation of metathioxen (I) gives 2-thiotolen-4-carboxylic acid is criticised. Repetition of the prep. of the acid there described as 4-bromo-3-methylthiophen-5-carboxylic acid, m.p. 195°, gave 4-bromo-3-methylthiophen-x-carboxylic acid, m.p. 219—220° (*Me* ester, m.p. 76°, which regenerates the acid on hydrolysis), reduced by Na–Hg to 3-methyldihydrothiophen-x-carboxylic acid, m.p. 79° (cf. *loc. cit.*). The author maintains that the α-Me is converted into CO_2H in the partial oxidation of (I) (cf. A., 1934, 81). H. G. M.

Dyes derived from acenaphthenequinone. V. 5-Methyl-1 : 8′-thionaphthenacenaphthenylindigos. S. K. Guha (J. Indian Chem. Soc., 1936, **13**, 94—97).—2-Hydroxy-5-methylthionaphthen with acenaphthenequinone and its derivatives in AcOH–conc. HCl gives 5-*methyl*-1 : 8′-*thionaphthenacenaphthenylindigo* (I), m.p. 305°, and its 3′-*Cl*-, m.p. 297°, 3′-*Br*-, m.p. 302°, and 1′-*OMe*-, m.p 300° (softens at 298°), derivatives. These dye wool (from acid bath) and cotton (from $Na_2S_2O_4$ vat) with lighter shades (of red) than the isomeric 4-Me compounds (A., 1934, 534). H. B.



(I.)

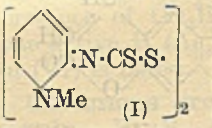
Bimolecular reduction of thioindigotindisulphonate.—See this vol., 800.

Phenoxthionine. I. Comparison of directive influences of oxygen and sulphur. C. M. Suter, J. P. McKenzie, and C. E. Maxwell (J. Amer. Chem. Soc., 1936, **58**, 717—720).—Phenoxthionine (I), m.p. 57·5—58°, obtained (cf. Ferrario, A., 1911, i, 555) from Ph_2O (10·4 mols.), S (8 mols.), and $AlCl_3$ (3·84 mols.) at 100° in 67—72% yield, with Br in CCl_4 gives the 2-*Br*-derivative (II), m.p. 59—60° (which could not be prepared from p-$C_6H_4Br{\cdot}OPh$ and S), and then the 2 : 8-Br_2-derivative, m.p. 92—93° [oxidised (30% H_2O_2, AcOH) to the 10 : 10-*dioxide* (III), m.p. 185—186°]. 4 : 4′-Dibromodiphenyl ether (IV) and $ClSO_3H$ (1 mol.) in CCl_4 followed by H_2O give the 2-sulphonic acid (*Na* salt), the *chloride*, m.p. 128—129°, of which with $AlCl_3$ in s-$C_2H_2Cl_4$ affords (III). (IV) and an excess of $ClSO_3H$ give the 2 : 2′-*disulphonyl chloride*, m.p. 241—243°, hydrolysed to the disulphonic acid (*Na* salt). (I), AcCl, and $AlCl_3$ in CS_2 afford 2-*acetylphenoxthionine*, m.p. 111—112° (phenylhydrazone, m.p. 93·5—94·5°; oxime, m.p. 142—143°), oxidised ($CaOCl_2$, dil. NaOH) to *phenoxthionine*-2-*carboxylic acid*, m.p. 260—262°, which was also obtained (in 8% yield) from the Grignard reagent (prepared only once) from (II) and CO_2. 2-*Benzoyl*-, m.p. 96—97°, and 2 : 8-*dibenzoyl*-, m.p. 197°, -*phenoxthionines* are prepared from (I), BzCl (1 mol.), and $AlCl_3$ in CS_2. (I) with 1 and 4 mols. of $ClSO_3H$ in CCl_4 gives phenoxthionine-2-sulphonic acid (*Na* salt; *chloride*, m.p. 127—128°; *amide*, m.p. 177—178°) and -2 : 8-disulphonic acid [*Na* and *Ag* salts; *chloride* (V), m.p. 142—143°, also obtained directly from (I) and $ClSO_3H$], respectively. (V) heated with PCl_5 affords a little of (probably) 2 : 8-dichlorophenoxthionine, m.p. 134—135° (Hilditch and Smiles, J.C.S., 1911, **99**, 408). In all the above reactions with (I), O has a greater directive influence than S. Contrary to Ferrario (*loc. cit.*), (I) could not be converted into diphenylene oxide by Cu at 250° or 285—290°. H. B.

Reactions of hydrogen with derivatives of pyrrole. F. K. Signaigo and H. Adkins (J. Amer. Chem. Soc., 1936, **58**, 709—716).—Pyrroles are more resistant to hydrogenation [H_2 (usually 200—300 atm.); Raney Ni or Cu–Cr oxide; EtOH, dioxan, methyl*cyclo*hexane, or no solvent] than any of the unsaturated ring compounds hitherto examined; reduction is, however, facilitated by an N-substituent (*e.g.*, Ph, CO_2Et). The following reductions are done with Ni: pyrrole to pyrrolidine (47% yield) at 180°; 3 : 5-dimethyl-2 : 4-diethylpyrrole to 3 : 5-*dimethyl*-2 : 4-*diethylpyrrolidine*, b.p. 186—188°, (70%) at 180°; 1-phenylpyrrole to 1-phenyl- (63%) and 1-*cyclo*hexyl-pyrrolidine (30%) at 135° (0 and 84%, respectively, at 180°); Et pyrrole-1-carboxylate to *Et pyrrolidine*-1-*carboxylate*, b.p. 98—99°/20 mm., (77%) at 160°; *Et pyrrole*-1 : 2-*dicarboxylate* (I), b.p. 132—134°/8 mm., to *Et pyrrolidine*-1 : 2-*dicarboxylate*, b.p. 133—134°/7·5 mm., (97—98%) at 50—85°. Acylpyrroles are converted (65—95% yield) into alkylpyrroles using Ni or (usually) Cu–Cr oxide at 135—175°. Thus, Et 4-acetyl-3 : 5-dimethylpyrrole-2-carboxylate gives Et 3 : 5-dimethyl-4-ethylpyrrole-2-carboxylate; Et and *Bu*$^{\gamma}$, m.p. 154—155° (prep. as A., 1933, 1303), 5-*acetyl*-2 : 4-*dimethylpyrrole*-3-*carboxylate* afford Et and *Bu*$^{\gamma}$ (II), m.p. 128—129°, 2 : 4-*dimethyl*-5-*ethylpyrrole*-3-*carboxylate*, respectively; Et 5-benzoyl-2 : 4-dimethylpyrrole-3-carboxylate furnishes Et 5-benzyl-2 : 4-dimethylpyrrole-3-carboxylate (III), m.p. 119—121°; 2 : 4-diacetyl-3 : 5-dimethylpyrrole (IV) (prep. as *loc. cit.*) yields 3-*acetyl*-2 : 4-*dimethyl*-5-*ethylpyrrole*, m.p. 157—158°, which then gives 3 : 5-dimethyl-2 : 4-diethylpyrrole. *C*-Carbethoxypyrroles undergo hydrogenolysis to the methylpyrroles with Cu–Cr oxide at 210—225°; further reduction to the methylpyrrolidines may then occur (with 3-CO_2Et, but not 2-CO_2Et, reduction precedes hydrogenolysis). Thus, Et 3 : 5-dimethyl-4-ethylpyrrole-2-carboxylate (V) gives 2 : 4 : 5-trimethyl-3-ethylpyrrole (VI) (30%) and -pyrrolidine (VII) (15%); Et 3 : 5-dimethylpyrrole-2 : 4-dicarboxylate (VIII) affords (according to H_2 absorbed) Et 2 : 4 : 5-trimethylpyrrole-3-carboxylate (IX) (33—55%) and 2 : 3 : 4 : 5-tetramethyl-pyrrole (X) (trace—13%) and -pyrrolidine (XI) (5—25%); (IX) furnishes (X) (2%) and (XI) (33%); Et 2 : 4-dimethyl-5-ethylpyrrole-3-carboxylate (XII) yields 3 : 4 : 5-*trimethyl*-2-*ethylpyrrolidine* (XIII), b.p. 147—151° (30%); Et 4-acetyl-3 : 5-dimethylpyrrole-2-carboxylate gives (V) (36%), (VI) (23%), and (VII) (29%); (I) affords 2-methylpyrrole (42%). Reduction of the above esters is also accompanied by *N*-ethylation (with EtOH produced during hydrogenolysis); this is better accomplished by reduction at (usually) 250° with Ni or Cu–Cr oxide in EtOH. Thus, Et pyrrole-2-carboxylate furnishes 1-ethyl- (10%; Ni) or 2-*methyl*-1-*ethyl-pyrrolidine*, b.p. 119—120° (90%; Cu); (XII) yields (XIII) (0—35%) and 3 : 4 : 5-*trimethyl*-1 : 2-*diethylpyrrolidine*, b.p. 183—184° (35—88%); (V) gives (according to H_2 consumed and catalyst) (VII) (0—8%), 4 : 5-dimethyl-1 : 3-diethyl- (37%), and 2 : 4 : 5-*trimethyl*-1 : 3-*diethyl-pyrrolidine*, b.p. 184—185° (37—80%); (VIII) affords 2 : 3 : 4 : 5-*tetramethyl*-1-*ethylpyrrolidine*, b.p. 163—165° (70%); (III) furnishes 3 : 4 : 5-trimethyl-1-ethyl-, b.p. 52—55°/23 mm. (17%) (*hydrochloride*), and 2-*benzyl*-3 : 4 : 5-*trimethyl*-1-*ethyl-pyrrolidine*, b.p. 139—141°/12 mm. (52%); (II) yields (XIII) (80%) (*N*-ethylation does not occur); (IV) gives 3 : 5-*dimethyl*-1 : 2 : 4-*triethylpyrrolidine*, b.p. 200—201° (50%); Et pyrrole-1-carboxylate affords 1-methyl- (27%) and 1-ethyl- (37%) -pyrrolidines. Further reduction [Cu–Cr oxide, EtOH, 200—250°, H_2 (varying amounts)] of Et pyrrolidine-1 : 2-dicarboxylate gives 2-methyl-1-ethyl- (XIV) (2—27%) and 1-*ethyl*-2-*hydroxymethyl-pyrrolidine* (XV), b.p. 82—84°/24 mm. (23—34%), and Et 2-hydroxymethylpyrrolidine-1-carboxylate, b.p. 134—135°/8 mm. (0—62%) [also reduced further to (XIV) (7%) and (XV) (32%)]. Much better yields of many of the above compounds are obtained by hydrogenolysis than by other methods. H. B.

Interaction of alkyl chlorosulphinates and pyridine in ethereal solution. W. GERRARD (J.C.S., 1936, 688—691).—When an alkyl chlorosulphinate, RO·SOCl, is mixed with C_5H_5N in Et_2O, an oily mixture of 1-alkylpyridinium chloride and 1-alkylpyridinium chlorosulphinate separates in quantity, leaving in the Et_2O about a 40% yield of alkyl chloride. With 1 mol. of chlorosulphinate per mol. of C_5H_5N, nearly one third of the base remained in the Et_2O, but with 0·5 mol. of the base, no C_5H_5N remained in the Et_2O, and the yield of alkyl chloride was somewhat larger. Two mechanisms for the reaction are suggested. The isolation and identification of the alkylpyridinium compounds have been effected through the ferrocyanides, $(C_5H_5NR)_2H_2Fe(CN)_6,2H_2O$: *ferrocyanide*; R=Me; Et, m.p. 150—151° (decomp.); Pr, m.p. 143° (decomp.); Bu, decomp. 165°; *iso*amyl; Pr$^{\beta}$, decomp. 145°; Bu$^{\beta}$, decomp. 150°; *derivatives* of C_5H_5NR : R=Me, picrate, m.p. 109°, aurichloride, m.p. 247°; Et, picrate, m.p. 89°, aurichloride, m.p. 141—142°, platinichloride, m.p. 201°; Pr, aurichloride, m.p. 128°; Bu, platinichloride, m.p. 202°, aurichloride, m.p. 117°; *iso*amyl, platinichloride, m.p. 203°, aurichloride, m.p. 139°; Pr$^{\beta}$, aurichloride, m.p. 144°; and Bu$^{\beta}$, aurichloride, m.p. 139—140°. F. R. S.

***N*-Methylpyridinethiouram disulphide.** K. S. TOPTSCHIEV (Compt. rend. Acad. Sci. U.R.S.S., *1936*, **1**, 115—118).—Oxidation of the methylpyridoneimide salt of its dithiocarbamic acid (A., 1935, 995) either with 10% I–EtOH at 0° or 3% H_2O_2 in aq. EtOH affords the *disulphide* (I), m.p. 142°, hydrolysed by boiling KOH–EtOH to *N*-methylpyridone, K_2S, and KCNS [from $(NH_2·CS·S·)_2$]. J. W. B.



(I)

Nicotinamide methiodide. P. KARRER and O. WARBURG (Biochem. Z., 1936, **285**, 297—298).—The hydrochloride, m.p. 233°, of the iminoethyl ether, the methylamide, m.p. 100°, the *N*-methylamidine, decomp. 235°, and the methoxymethochloride of the amide of nicotinic acid do not react (at p_H 8 and room temp.) with $Na_2S_2O_4$; glucosido-1-pyridinium iodide reacts slowly yielding a substance not identical with reduced H-transporting co-enzyme (I). The methiodide of nicotinamide (II) reacts as quickly as does (I) yielding a substance identical with reduced (I). (I) contains 13·3% of (II). W. McC.

Synthesis in the indole group. XV. Synthesis of bufotenin methyl ether (5-methoxy-*NN*-dimethyltryptamine) and bufotenin. T. HOSHINO and K. SHIMODAIRA (Bull. Chem. Soc. Japan, 1936, **11**, 221—224).—Bufotenin Me ether (I) is synthesised in a manner similar to that used for its Et ether (A., 1935, 1378). 5-*Methoxy*-3-*indolylacetic acid*, m.p. 146—147° (from the nitrile), gives its *Et* ester, b.p. 202—203°/4 mm., m.p. 97—98°, reduced to 5-*methoxytryptophol*, b.p. 194°/4 mm. (*picrate*, m.p. 117—118°), from which are obtained 5-*methoxy*-3-β-*bromoethylindole* and 5-*methoxy*-NN-*dimethyltryptamine* (I), m.p. 66—67° [*picrate*, m.p. 176—177°; *mono*-, m.p. 170—171°, and *di-picrate*, m.p. 103—104° (lit. m.p. 84°), of the methiodide], demethylated by $AlCl_3$ to bufotenin. When heated with MeI–EtOH–anhyd. Na_2CO_3 5-methoxytryptamine affords the methiodide of (I), converted by AgCl into the *methochloride*, m.p. 144°, which gives (I) when heated at 240—250°. J. W. B.

Stereoisomerism of 6-methyldecahydroquinoline. S. Fujise and M. Iwakiri (Bull. Chem. Soc. Japan, 1936, **11**, 293—294).—Reduction of 6-methylquinoline (PtO_2–H_2 in AcOH, 50°) affords trans- (I), m.p. 68—69°, b.p. 211·5—212° (*hydrochloride*, m.p. 265°; *hydrobromide*, m.p. 244—245°; *aurichloride*, m.p. 117—119°; *platinichloride*, m.p. 171·5—172·5°; *Bz*, m.p. 95—99°, and p-*nitrobenzoyl*, m.p. 124·5—125°, derivatives), and cis-6-*methyldecahydroquinoline*, b.p. 212—212·5° [*hydrochloride*, m.p. 263—264°; *hydrobromide*, m.p. 252—253°; *aurichloride*, m.p. 152—153°; *platinichloride*, m.p. 230° (decomp.); p-*nitrobenzoyl*, m.p. 138—139°, and liquid Bz derivative]. Resolution of (I) with *d*-bromocamphorsulphonic acid gives the d-*trans-form*, m.p. 92—93°, $[\alpha]_D^{14·5}$ +4·8° in EtOH. The reduced 6-methylquinoline, m.p. 44° (Finger *et al.*, A., 1909, i, 512), must be impure (I). J. W. B.

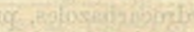
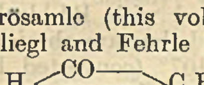
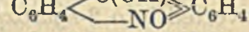
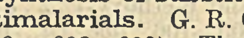
4-Hydroxyquinoline-3-aldehyde. Preparation of 4-hydroxyquinoline (kynurine). B. Bobrański (Ber., 1936, 69, [*B*], 1113—1117).—4-Hydroxyquinoline (prep. from quinoline through the oxide and 4-chloroquinoline described) is converted by NaOH and $CHCl_3$ into 4-*hydroxyquinoline*-3-*aldehyde*, m.p. 273° (decomp.), in about 10% yield. It is a very weak base which does not reduce NH_3–Ag_2O or Fehling's solution. The *phenylhydrazone*, m.p. 244—245° (decomp.), and *oxime*, m.p. 222—223° (decomp.) when rapidly heated and m.p. 241° after re-solidification, are described. H. W.

2-Phenylquinoline series. K. Feist and M. Kuklinski (Arch. Pharm., 1936, **274**, 310—315; cf. this vol., 735).—The NH_2 of 4-amino-2-phenylquinoline (I) is relatively unreactive. (I) and NH_4CNS in very dil. HCl give the *thiocarbamide*, m.p. 277°, but C_3H_5·CNS and PhCNS give only poor yields of *allyl-*, m.p. 279°, and *phenyl-carbamide*, derivatives, m.p. 150°. (I), S, and NaOH in hot CS_2–EtOH give only a little 2-*phenylquinolyl*-4-*thiourethane*, m.p. 151°, and probably H_2S; 6-amino-2-methylpyridine gives mainly thiocarbamide with a little thiourethane. (I) and the aldehyde, when melted together, afford the o-*methoxybenzylidene*, m.p. 136°, and *salicylidene* derivative (II), m.p. 138°, but *o*- (III) and *p*-NO_2·C_6H_4·CHO (IV) and *p*-NMe_2·C_6H_4·CHO do not react. (II) yields (H_2–Pd-black in Et_2O) 4-*benzylamino-2-phenylquinoline*, m.p. 204°. (I) also does not react with (III), (IV), PhCHO, *o*-OH·C_6H_4·CHO, or piperonal in anhyd. HCO_2H.
R. S. C.

Catalytic dehydrogenation of 3-phenyltetrahydro*iso*quinolines. B. Reichert and W. Hoffmann (Arch. Pharm., 1936, **274**, 281—283).—6 : 8-Methylenedioxy-3-phenyl- and -3-4′ : 5′-methylenedioxyphenyl-, 6-methoxy- and 6 : 7-dimethoxy-3-phenyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline are quantitatively dehydrogenated by 10—25% of Pd-black at 170—210°, the reaction being favoured by the 3-Ph. 6 : 7-*Dimethoxy-*, m.p. 128°, and 6-*methoxy*-3-*phenyl*iso*quinoline*, m.p. 101°, are described.
R. S. C.

Synthesis of alkoxy- and hydroxy-carbazoles. T. Hoshino and K. Takiura (Bull. Chem. Soc. Japan, 1936, **11**, 218—220).—Dehydrogenation of tetrahydrocarbazoles, prepared by Borsche's method (A., 1908, i, 365), is best effected with Pd-black–CHPh:CH·CO_2H at 150—200°, and thus are obtained carbazole, 3-*ethoxy-*, m.p. 106—107° (converted by NH_2Ph,HCl at 220° in CO_2 into 3-*hydroxy-*, m.p. 256—257°), 7-*ethoxy*-1 : 2 : 3 : 4-*tetrahydro-*, m.p. 120°, 2-*ethoxy-*, m.p. 216—217°, converted into 2-*hydroxy-*, m.p. 273—274°, -*carbazole*. *cyclo*Hexanone-*p*-phenetylhydrazone has m.p. 77° and 6-ethoxy-1 : 2 : 3 : 4-tetrahydrocarbazole, m.p. 105—106° (*loc. cit.*, m.p. 87—88°). J. W. B.

4 : 5-Di-*m*-aminophenylcarbazole. S. Sako (Bull. Chem. Soc. Japan, 1936, **11**, 144—157).—3-Nitro-2-acetamidodiphenyl with H_2SO_4–HNO_3 (*d* 1·52) $< 2°$ gives its 4′-NO_2-derivative, m.p. 207·5°, hydrolysed (boiling EtOH–conc. HCl) to 3 : 4′-*dinitro-2-amino-*, m.p. 196—197° (oxidised to *p*-CO_2H·C_6H_4·NO_2), converted through its diazo-compound into 2-*iodo*-3 : 4′-*dinitro-*, m.p. 139—140°, and reduced by Na_2S–aq. EtOH to 3-*nitro*-2 : 4′-*diamino-diphenyl*, m.p. 156—157°, converted by Ac_2O–C_6H_6 into its 4′-*Ac* derivative, m.p. 174—175°, converted (Sandmeyer) into the 4′-*Ac* derivative, m.p. 239°, of 2-*iodo-3-nitro-4′-aminodiphenyl* (I), m.p. 126—127° [*hydrochloride*; p-*toluenesulphonyl* derivative (II), m.p. 136—137°], which is obtained by hydrolysis with EtOH–conc. HCl. Addition of (I) to HNO_3 (*d* 1·456, essential) at 0° affords 2-*iodo*-3 : 3′-*dinitro-4′-acetamidodiphenyl*, m.p. 196—197°, hydrolysed to the 4′-NH_2-compound (III), m.p. 178—178·5°. (I) with HNO_3 (*d* 1·52) gives the 3 : 3′ : 5′-$(NO_2)_3$ derivative, m.p. 263—264°, hydrolysed to 2-*iodo*-3 : 3′ : 5′-*trinitro-4-aminodiphenyl*, m.p. 220—221°, also obtained by nitration of (II) and subsequent hydrolysis. Deamination of (III) by the diazo-reaction affords 2-*iodo*-3 : 3′-*dinitrodiphenyl*, m.p. 130—131°, b.p. 239°/6 mm., converted by Cu powder at 190—195° into 2 : 2′-*dinitro*-6 : 6′-*di*-m-*nitrophenyl-*, m.p. 259·5—260°, reduced ($SnCl_2$–AcOH–HCl) to 2 : 2′-*diamino*-6 : 6′-*di*-m-*aminophenyldiphenyl*, m.p. 169—170°, converted by 0·5*N*-HCl (N_2 atm.) at 200—205° into 4 : 5-*di*-m-*aminophenylcarbazole* (IV), softens 175°, m.p. 180—182° [*dihydrochloride*, +$2H_2O$; Ac_2, m.p. 257—258°, and *di*-l-*menthoxyacetyl* derivative (V), m.p. 190—191°, $[\alpha]_D$ −22·27° in EtOH, +14·2° in C_6H_6]. Spatial considerations suggest that (IV) should exist in *cis*- and *trans*-forms, the latter being resolvable, but attempts to resolve (IV) with *d*-camphorsulphonic acid or *d*-tartaric acid failed, and hydrolysis of the *l*-menthoxyacetyl group from (V) was unsuccessful.
J. W. B.

Acridine. XIII. *ms*-Acridine derivatives. IV. "Acridol" and the tautomerism, *N*-hydroxyacridone–5-hydroxyacridine 10-oxide. K. Lehmstedt and H. Klee (Ber., 1936, 69, [*B*], 1155—1158; cf. A., 1935, 1251).—Acridine *N*-oxide identical with " acridol " is converted by $NaHSO_3$ and HCN into acridine (I) and 5-cyanoacridine, respectively; since in these reactions it behaves similarly to (I) it must be formulated  $C_6H_4{<}\genfrac{}{}{0pt}{}{CH}{NO}{\gg}C_6H_4$ not  In agreement with Kliegl and Brösamle (this vol., 343) the hydroxyacridone of Kliegl and Fehrle (A., 1914, i, 867) is regarded as  $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{N(OH)}{>}C_6H_4$ which can become tautomerised to  $C_6H_4{<}\genfrac{}{}{0pt}{}{C(OH)}{NO}{\gg}C_6H_4$. H. W.

Synthesis of substituted acridines as possible antimalarials. G. R. Clemo and W. Hook (J.C.S., 1936, 608—609).—The p-*toluenesulphonamide* of 1-*methylamino*-5 : 10-*dihydroacridine*, m.p. 170°, is hydrolysed (H_2SO_4) to 1-*methylaminoacridine*, m.p. 75°. 1-(β-*Diethylaminoethyl*)*aminoacridine*, b.p. 180°/1 mm. [*dipicrate*, m.p. 192°; *monopicrate*, m.p. 151°; *dihydrochloride* ($+2H_2O$), m.p. 104°], is obtained from 1-aminoacridine, $CH_2Cl{\cdot}CH_2{\cdot}NEt_2,HCl$, and NaOAc, and also by hydrolysing the *p*-toluenesulphonamide of 1-(β-*diethylaminoethyl*)*amino*-5 : 10-*dihydroacridine*, m.p. 88°. α-Diethylamino-δ-hydroxypentane and $SOCl_2$ followed by NaOH give δ-chloro-α-diethylaminopentane (*methiodide*, m.p. 116°), which is isomerised to a solid [*picrate*, m.p. 270° (decomp.)]. 1-Aminoacridine (*monopicrate*, m.p. 220°), *p*-nitrobenzyl bromide, and NaOAc give 1-(p-*nitrobenzyl*)-*aminoacridine*, m.p. 170°, reduced to the 1-p-NH_2-compound [*dihydrochloride* ($+2H_2O$), m.p. 168°; *dipicrate*, m.p. 178° (decomp.)]. F. R. S.

Manufacture of acridine derivatives [pharmaceuticals].—See B., 1936, 524.

Creatinine derivatives. II. W. R. Cornthwaite, S. Lazarus, R. H. Snellings, jun., and C. E. Denoon, jun. (J. Amer. Chem. Soc., 1936, 58, 628—629; cf. A., 1935, 352).—Creatinine and the appropriate RCHO at 150—180° give 5-o- (I), m.p. 241°, and -p-, m.p. 248—249° (decomp.), -*anisylidene*-, 5-o-*ethoxybenzylidene*- (II), m.p. 236° (decomp.), 5-p-*hydroxybenzylidene*-, m.p. 289° (cf. Deulofeu and Mendivelzua, A., 1935, 850), 5-p-*tolylidene*- (III), m.p. 285° (decomp.), 5-o-*chlorobenzylidene*- (IV), m.p. 242° (decomp.; sealed tube), 5-*piperonylidene*- (V), m.p. 274° (decomp.; sealed tube), and 5-γ-*phenylpropylidene*-, m.p. 225—230°, -*creatinine*. (I)—(V) are accompanied by *products*, m.p. 292°, 297°, 309°, 270°, and 327°, respectively, which are (probably) triarylidenecreatinines; that from *o*-$OEt{\cdot}C_6H_4{\cdot}CHO$ is also produced from (II) and an excess of the aldehyde at 175°. H. B.

Tertiary alkylbarbituric acids. A. W. Dox and W. G. Bywater (J. Amer. Chem. Soc., 1936, 58, 731—732).—$CHBu^{\gamma}(CO_2Et)_2$, b.p. 205—210°/750 mm. [obtained in 6·4% yield from $CHNa(CO_2Et)_2$ and $Bu^{\gamma}Br$ in EtOH at 5°—room temp.], and $CEtBu^{\gamma}(CO_2Et)_2$, b.p. 244—248° [formed in 3·8% yield from $CHEt(CO_2Et)_2$ (I), $Bu^{\gamma}Br$, and Na powder in dry PhMe], with $CO(NH_2)_2$ in EtOH–NaOEt give 5-tert.-*butyl*- (II), m.p. 230—231°, and impure 5-*ethyl*-5-tert.-*butyl*- (III), m.p. 191·5—192·5°, -*barbituric acid*, respectively. 5-*Ethyl*-5-tert.-*amylbarbituric acid* (IV), m.p. 196·5—197·5°, is similarly prepared from Et ethyl*tert.*-amylmalonate, b.p. 93—96°/1·5 mm. [formed in 4·6% yield from (I), *tert.*-amyl bromide, and EtOH–NaOEt at room temp.]. Contrary to expectation, (III) and (IV) are not more active than the isomeric 5-*sec.*-alkyl derivatives. (II) is inactive. H. B.

Nitrogen-substituted barbituric acids. D. Nightingale and C. H. Alexander (J. Amer. Chem. Soc., 1936, 58, 794—796).—1-Aryl- and 1 : 3-diarylbarbituric acids are prepared from $CH_2(COCl)_2$ and $NH_2{\cdot}CO{\cdot}NHAr$ or $CO(NHAr)_2$ (Whiteley, J.C.S., 1907, 91, 1330); their 5 : 5-di-*p*-nitrobenzyl derivatives are obtained by Lyons and Dox's method (A., 1929, 453), whilst the 5-anilinomethylene derivatives, which are recommended for identification, are formed from the acids and NHPh·CH:NPh in EtOH. The following are described: 1-phenyl- (5-*cinnamylidene*, decomp. 271°, 5 : 5-*di*-p-*nitrobenzyl*, m.p. > 295°, and 5-*anilinomethylene*, m.p. 271°, derivatives); 1-p-*tolyl*-, m.p. 244° (5-*cinnamylidene*, decomp. 275°, 5 : 5-*di*-p-*nitrobenzyl*, m.p. 245°, and 5-*anilinomethylene*, m.p. 290°, derivatives); 1-p-*phenetyl*-, m.p. 211° (5-*cinnamylidene*, decomp. 258°, 5 : 5-*di*-p-*nitrobenzyl*, m.p. 240°, and 5-*anilinomethylene*, m.p. 248°, derivatives); 1 : 3-diphenyl- (5 : 5-*di*-p-*nitrobenzyl*, m.p. > 300°, and 5-*anilinomethylene*, m.p. 228°, derivatives); 1 : 3-*di*-o-*tolyl*-, m.p. 171° (5-*cinnamylidene*, decomp. 223°, 5 : 5-*di*-p-*nitrobenzyl*, m.p. > 300°, and 5-*anilinomethylene*, m.p. 198°, derivatives); 1 : 3-*di*-p-*tolyl*-, m.p. 213° (5-*cinnamylidene*, decomp. 260°, 5 : 5-*di*-p-*nitrobenzyl*, m.p. > 300°, and 5-*anilinomethylene*, m.p. 258°, derivatives); 1 : 3-*di*-p-*phenetyl*-, m.p. 167° (5-*anilinomethylene* derivative, m.p. 207°); 1 : 3-diphenyl-2-thio- (5-*anilinomethylene* derivative, m.p. > 300°), and 1 : 3-*di*-o-*tolyl*-2-*thio*-*barbituric acid*, m.p. 217° (5-*cinnamylidene*, decomp. 248°, and 5-*anilinomethylene*, m.p. 237°, derivative). H. B.

Synthesis of glyoxaline derivatives from α-amino-acids. III. Synthesis of two homologues of histamine. S. Akabori and T. Kaneko. **IV. Synthesis of histamine.** S. Akabori and S. Numano (Bull. Chem. Soc. Japan, 1936, **11**, 208—213, 214—217).—III. Reduction of arginine Et ester dihydrochloride with Na–Hg–EtOH–5*N*-HCl at −12° to −17° and treatment of the product with NH_4SCN affords 2-*thiol*-5-γ-*guanidinopropylglyoxaline hydrochloride* (I), m.p. 236·5—237·5° (decomp.), converted by aq. $FeCl_3$–phosphotungstic acid into 5-γ-*guanidinopropylglyoxaline* [*picrate*, m.p. 258° (decomp.); *flavianate*, m.p. 248° (decomp.)], isolated as its *dinitrate* (II), m.p. 183·5—184° (decomp.). Hydrolysis of (I) with $Ba(OH)_2$ gives 2-thiol-5-γ-aminopropylglyoxaline (not isolated), converted by $FeCl_3$–phosphotungstic acid into 5-γ-*aminopropylglyoxaline* (III), isolated as its *picrate*, m.p. 244—244·5° (decomp.), also obtained by hydrolysis of (II). Similarly lysine Et ester dihydrochloride is converted successively into 2-*thiol*-5-δ-*amino*-n-*butyl*-, m.p. 220·5—221·5° (decomp.) [*hydrochloride*, m.p. 212—214° (decomp.); *picrate*, m.p. 154—155° (decomp.)], and 5-γ-*amino*-n-*butyl*-*glyoxaline* (IV), b.p. 204°/6 mm., m.p. 51—53° [*oxalate*, m.p. 168·5—170° (decomp.); *picrate*, m.p. 197·5—198·5° (decomp.)]. The physiological action (non-pregnant dogs) of (III) is $<$, and that of (IV) $\ll$, that of histamine (V).

IV. *Et hydantoinpropionate*, m.p. 78—82°, is converted through the *hydrazide*, m.p. 164—167°, *azide*, decomp. 69—70°, into *Et* β-*hydantoinylethylcarbamate*, m.p. 82—88°, hydrolysed by $Ba(OH)_2$ to αγ-diaminobutyric acid hydrochloride, the *Et* ester, m.p. 173—175° (decomp.), of which is converted as above into 2-*thiolhistamine hydrochloride*, m.p. 245·5—247°, and (V). J. W. B.

Ethylene oxamide (2 : 3-diketopiperazine). J. van Alphen (Rec. trav. chim., 1935, **54**, 937—939).—2 : 3-*Diketopiperazine* (I), m.p. 285°, is obtained when $Et_2C_2O_4$ and ethylenediamine hydrate [corresponding *dioxalate*, m.p. 207° (decomp.)] are added very gradually to much abs. EtOH (cf. lit.). In H_2O they give β-*aminoethyloxamic acid*, m.p. about 320° (decomp.). (I) forms the 1 : 4-$(NO_2)_2$-derivative, m.p. about 150° (decomp.). H. G. M.

Pyrimidines. (A) Molecular rearrangement of 2-ethylthiol-6-thiocyano-4 : 5-dimethylpyrimidine. (B) Synthesis of 4 : 5-dimethylcytosine. Y. F. Chi and Y. S. Kao. **(C) Molecular rearrangement of 2-ethylthiol-6-thiocyano-4-phenylpyrimidine.** Y. F. Chi, Y. S. Kao, and Y. T. Huang (J. Amer. Chem. Soc., 1936, **58**, 769—771, 772, 773—774; cf. A., 1934, 85).—(A) 6-*Hydroxy*-4 : 5-*dimethyl*-2-*thiopyrimidine* (I), m.p. 279—280° [from $CS(NH_2)_2$ and $CHMeAc{\cdot}CO_2Et$ in EtOH–NaOEt], with EtI, MeI, and $CH_2Cl{\cdot}CO_2Et$ in EtOH–NaOEt gives 2-ethylthiol- (II), m.p. 155—156°, 2-*methylthiol*-, m.p. 225—227°, and 2-*carbethoxymethylthiol*-, m.p. 132—133° [and thence 2-*carboxymethylthiol*- ($+H_2O$), m.p. 128—129°], -4 : 5-*dimethyluracil*, respectively. 4 : 5-Dimethyluracil, m.p. 294—296°, is obtained from (I) and aq. $CH_2Cl{\cdot}CO_2H$ or from (II) and aq. HBr. (II) and $POCl_3$ give 6-*chloro*-2-*ethylthiol*-4 : 5-*dimethylpyrimidine* (III), b.p. 142—144°/10 mm., which with KCNS in EtOH affords 2-*ethylthiol*-6-*thiocyano*-4 : 5-*dimethylpyrimidine* (IV), b.p. 160°/1·5 mm., m.p. 64·5—65·5°, converted by $SH{\cdot}CH_2{\cdot}CO_2H$ into 2-*ethylthiol*-4 : 5-*dimethyl*-6-*thiopyrimidine*, m.p. 187—188° [also formed from (III) and NaHS]. (IV) heated in xylene for 20 hr. at the b.p. rearranges partly into 2-*ethylthiol*-6-*thiocarbimido*-4 : 5-*dimethylpyrimidine* (V), b.p. 150—152°/1·5 mm., m.p. 29·5—30°, which with NH_2Ph and conc. aq. NH_3 in light petroleum gives the 6-*phenylthiocarbamido*-, m.p. 139—141°, and 6-*thiocarbamido*-, m.p. 209—210°, derivatives, respectively. (V) with MeOH, EtOH, and $Pr^{\alpha}OH$ affords the corresponding *thiourethanes*, m.p. 75—76°, 129—130°, and 61—63°, respectively.

(B) 6-*Amino*-2-*ethylthiol*-4 : 5-*dimethylpyrimidine*, m.p. 92—93° [from (III) (above) and conc. EtOH–NH_3 at 140—150°], is hydrolysed (48% HBr) to 4 : 5-*dimethylcytosine* ($+H_2O$), m.p. >300° [*hydrobromide*, m.p. 291° (decomp.) (sinters at 278°)].

(C) 2-*Ethylthiol*-6-*thiocyano*-4-*phenylpyrimidine* (VI), b.p. 204°/1·5 mm., m.p. 88—89° [from the 6-Cl-derivative (VII) and KCNS in EtOH], is converted by $SH{\cdot}CH_2{\cdot}CO_2H$ into 2-*ethythiol*-4-*phenyl*-6-*thiopyrimidine*, m.p. 206—207°, also prepared from (VII) and EtOH–NaHS. (VI) heated in PhMe at 160—170° (sealed tube) for 10 hr. rearranges to 2-*ethylthiol*-6-*thiocarbimido*-4-*phenylpyrimidine* (VIII), b.p. 215—218°/2 mm., which with NH_2Ph and NH_3 (as above) gives the 6-*phenylthiocarbamido*-, m.p. 215—216°, and 6-*thiocarbamido*-, m.p. 212—213°, derivatives, respectively. (VIII) with MeOH, EtOH, $Pr^{\alpha}OH$, and $Bu^{\alpha}OH$ affords the corresponding *thiourethanes*, m.p. 130—131°, 115—116°, 97—98°, and 89—90°, respectively. (IV) and (VI) do not react with NH_3, NH_2Ph, or alcohols. H. B.

1-Arylindazoles. II. W. Borsche and L. Bütschli (Annalen, 1936, **522**, 285—298).—The p-*tolylhydrazone*, m.p. 178—179°, p-*acetylphenylhydrazone*, m.p. 163—164°, p-*carboxyphenylhydrazone*, m.p. 262° (decomp.), 2 : 4-*dichlorophenylhydrazone*, m.p. 204°, 2 : 4 : 6-*trichlorophenylhydrazone*, m.p. 173—174°, and *mesitylhydrazone*, m.p. 137—138°, of Me 2 : 4-dinitrophenylglyoxylate are prepared (method: A., 1934, 784) from ArN_2Cl and $2:4\text{-}(NO_2)_2C_6H_3{\cdot}CH_2{\cdot}CO_2Me$ and converted (*loc. cit.*) into 6-nitro-1-*p*-tolyl-, m.p. 268° (decomp.) (*Me* ester, m.p. 191—192°), -1-p-*acetylphenyl*-, m.p. 233° (decomp.), -1-p-*carboxyphenyl*-, m.p. 300° (decomp.), -1-2′ : 4′-*dichlorophenyl*-, m.p. 262° (decomp.), -1-2′ : 4′ : 6′-trichlorophenyl-, decomp. 236° (*Me* ester, m.p. 190°), and -1-mesityl- (*Me* ester, m.p. 164°) -indazole-3-carboxylic acids, respectively. 6-*Nitro*-1-p-*tolyl*- (I), m.p. 134—135°, and -1-*mesityl*-, m.p. 109—110°, -*indazoles* are described. PhN_2Cl and $2:4\text{-}(NO_2)_2C_6H_3{\cdot}CH_2{\cdot}COPh$ (A., 1909, i, 232) in MeOH–C_5H_5N give α-*Ph* β-2 : 4-*dinitrophenyl diketone*-β-*phenylhydrazone*, m.p. 209° (decomp.) [corresponding anisylhydrazone, m.p. 175—176° (decomp.)], convertible into 6-*nitro*-3-*benzoyl*-1-*phenylindazole*, m.p. 212—214° (1-4′-OMe-derivative, m.p. 199—200°), also obtained from the chloride, m.p. 191°, of 6-nitro-1-phenylindazole-3-carboxylic acid (*anilide*, m.p. 220—221°), C_6H_6, and $AlCl_3$. A phenylhydrazone could not be prepared from 2 : 4-*dinitrobenzophenone*, m.p. 172° [from $2:4\text{-}(NO_2)_2C_6H_3{\cdot}COCl$, C_6H_6, and $AlCl_3$]. $2:4\text{-}(NO_2)_2C_6H_3{\cdot}CO_2H$ could not be prepared by oxidation (CrO_3, H_2SO_4) of $2:4\text{-}C_6H_3Me(NO_2)_2$; in one case, some 2 : 4-*dinitrophenyl* 2 : 4-*dinitrobenzyl ketone* (?) was obtained. Reduction (H_2, Pd–C, MeOH) of (I) gives 6-amino-1-*p*-tolylindazole (hydrochloride, decomp. 255—257°; *Bz* derivative, m.p. 213—214°) [converted by diazotisation and subsequent treatment with H_3PO_2 into 1-p-*tolylindazole* (II), m.p. 70°] and some of the *azoxy*-derivative, m.p. 200°. 6-Amino-3-acetyl-1-phenylindazole, m.p. 226—228° (*Bz* derivative, m.p. 192°), prepared from the 6-NO_2-compound, is similarly converted into 3-*acetyl*-1-*phenylindazole*, m.p. 84—85° (*oxime*, m.p. 137°; 2 : 4-*dinitrophenylhydrazone*, m.p. 263°), which with PhCHO in MeOH–NaOH gives 3-*cinnamoyl*-1-*phenylindazole*, m.p. 149—150°. Me 6-nitro-1-phenylindazole-3-carboxylate (III) (modified prep.) is similarly reduced to the NH_2-ester, m.p. 115° (*Bz* derivative, m.p. 201°), deaminated (as above) to the Me ester (IV), m.p. 81°, of 1-*phenylindazole*-3-*carboxylic acid*, m.p. 181° (*anilide*, m.p. 127—128°); the chloride, m.p. 147—148°, of this with C_6H_6 and $AlCl_3$ affords 3-*benzoyl*-1-*phenylindazole*, m.p. 148—149° (2 : 4-*dinitrophenyl*-

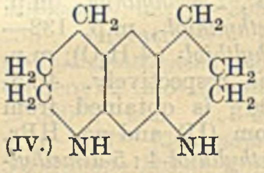
hydrazone, m.p. 215°). 1-Phenylindazole (V) and 86% HNO_3 give $(NO_2)_4$-derivatives, m.p. 226—228° and 238—241°; with KNO_3+conc. H_2SO_4 (method *a*) a $(NO_2)_2$-derivative, m.p. 253°, results. (II) affords (*a*) a $(NO_2)_2$-derivative, m.p. 215°. 6-Nitro-1-phenylindazole and fuming HNO_3 give a $(NO_2)_4$-compound, m.p. 220—223°; (*a*) leads to 6 : 4′-*dinitro*-1-*phenylindazole*, m.p. 265° [also obtained by decarboxylation of (VI) (below)], which is reduced (as above) to the $(NH_2)_2$-derivative, m.p. 207—209° (becoming red). Contrary to Strassmann (A., 1890, 781), a $(NO_2)_4$-compound, m.p. 225—226°, is formed from (III) and fuming HNO_3; (*a*) affords the *Me* ester, m.p. 269—270°, of 6 : 4′-dinitro-1-phenylindazole-3-carboxylic acid (VI), m.p. 275° (decomp.). (V) and Br in AcOH at room temp. give (probably) the 3 : 5 : 4′-Br_3-derivative, m.p. 181°; (II) and (IV) similarly yield the 3 : 5-Br_2-, m.p. 132—134°, and 5 : 4′-Br_2-, m.p. 182—183°, derivatives, respectively. Reduction ($SnCl_2$, AcOH–HCl) of (III) affords some 6-amino-1-phenylindazole-3-carboxylic acid (cf. Schulhöfer, A., 1891, 1231), also obtained from the 6-NO_2-acid and alkaline $Na_2S_2O_4$. An *azoxy*-compound, $C_{30}H_{34}O_9N_8$, m.p. 243—244° (decomp.), is formed by reduction (H_2, Pd–C, MeOH) of Me 2 : 4-dinitrophenylglyoxylate phenylhydrazone. H. B.

Pyrogenic rearrangement of 3-2-pyridylpyrrole. A. G. Oosterhuis and J. P. Wibaut (Rec. trav. chim., 1936, **55**, 348—349).—Under the conditions of pyrolysis of *N*-2-pyridylpyrrole (I) to 2- (II) and 3-2-pyridylpyrrole (III) (A., 1926, 1260; Tschitschibabin *et al.*, A., 1925, i, 1174), (III) is converted into (II) but not (II) into (III). Hence no (III) is found in the products if the vapour of (I) is passed too slowly through the reaction tube. J. W. B.

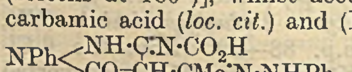
Quinoxaline colours. K. Yamada, T. Noguchi, and K. Oiwa (Bull. Chem. Soc. Japan, 1936, **11**, 225—231).—The solubility, colour reactions, and dyeing properties of the quinoxaline dyes obtained by condensation (in AcOH) of phenanthraquinone with o-$NH_2 \cdot C_6H_4 \cdot NHPh$ (I) (*chloride*, +0·5$ZnCl_2$, *bromide*, and *iodide*, all m.p. > 285°) and o-$NH_2 \cdot C_6H_4 \cdot NHMe$ (*chloride*, +0·5$ZnCl_2$, decomp. 200—205°; *bromide*, decomp. 216—217°; *iodide*, decomp. 195—200°), and of naphthoquinone with (I) (*chloride*, +0·5$ZnCl_2$, decomp. 278—279°; *bromide*, decomp. 281—282°; *iodide*, decomp. 220—221°) are tabulated. J. W. B.

Synthesis of α-picolyl*iso*quinolines as possible antimalarials. I. G. R. Clemo, H. McIlwain, and W. McG. Morgan (J.C.S., 1936, 610—611).—Et pyridyl-2-acetate and 3 : 4-methylenedioxy-β-phenylethylamine condense to *pyridyl*-2-*aceto*-3′ : 4′-*methylenedioxy*-β-*phenylethylamide*, m.p. 89°, which with $POCl_3$ forms 6 : 7-*methylenedioxy*-1-α-*picolyl*-3 : 4-*dihydro*iso*quinoline*, m.p. 105° [*dihydrochloride* (+EtOH), m.p. 210°; *picrate*, m.p. 210°]. This compound is reduced with Zn–H_2SO_4 to 6 : 7-*methylenedioxy*-1-α-*picolyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline* (I), b.p. 215°/1 mm. [*picrate*, m.p. 175°; *hydrochloride* (+H_2O), m.p. 205°], and with PtO_2–H_2 to the -α-*pipecolyl* compound, b.p. 210°/1 mm. (*picrate*, m.p. 236°; *hydrochloride*, m.p. 293°). (I) is dehydrogenated (Pd–C) to α-picoline and 6 : 7-methylenedioxy*iso*quinoline, isolated as the *picrate*, m.p. 206°. F. R. S.

Nitrogenous heterocyclic rings. XXIII. Reduced *lin.*-*m*-benzodipyridine. P. Ruggli and A. Staub (Helv. Chim. Acta, 1936, **19**, 439—448; cf. this vol., 614).—m-$C_6H_4(CH{:}CH \cdot CO_2H)_2$ (I) and HNO_3 (*d* 1·51) at 0° give only 4-*nitrophenylene*-1 : 3-*diacrylic acid* (II), m.p. 268—269° (decomp.), reduced by $FeSO_4$–aq. NH_3 or, better, H_2–Ni in AcOH at 40—50° to the 4-NH_2-*acid*, decomp. > 300°. Absence of ring-closure proves the *trans*-nature of the ethylenic linking. The Me_2 ester (III) of (I) with HNO_3 at −5° to 0° gives the Me_2 ester, m.p. 162° (*Ac* derivative, m.p. 215°), of (II), hydrogenation (Ni; aq. EtOH; 75°) of which gives 70% of *Me* β-*dihydrocarbostyril*-6-*propionate*, m.p. 134°, hydrolysed by acid or alkali to the corresponding *acid*, m.p. 234°. Hydrogenation (Ni; EtOH–EtOAc–H_2O) of (III) gives 95% of Me_2 *m*-phenylenedipropionate, m.p. 50—52°, converted by HNO_3 (*d* 1·52) at ≯ 0° into the 4 : 6-$(NO_2)_2$-ester, m.p. 71°, which with H_2–Ni in EtOH–EtOAc–H_2O gives by partial ring-closure *Me* β-7-*aminodihydrocarbostyril*-6-*propionate*, cryst. (*Ac* derivative, m.p. 245—246°). When heated at 250—270° or, better (90—100%), with conc. HCl, this gives 2 : 7-*diketo*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydro*-lin.-m-*benzodipyridine* [1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-*pyridono*-5′ : 6′-6 : 7-*dihydrocarbostyril*], sublimes at about 300°, which with HI–red P (not other reagents) at 185° yields 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydro*-lin.-m-*benzodipyridine* [1′ : 2′ : 3′ : 4′-*tetrahydropyridino*-5′ : 6′-6 : 7-ar-*tetrahydroquinoline*] (IV), m.p. 114°, b.p. 210°/vac. [*hydriodide*, m.p. 307°; *hydrochloride*; *Ac*$_2$, m.p. 143°, *Bz*$_2$, m.p. 209°, and $(NO_2)_2$-derivative, m.p. 187°; *picrate*, m.p. 210—215° (decomp. from 164—170°)], or, if less P is used, mainly the 2-*keto*-derivative of (I) [1′ : 2′ : 3′ : 4′-*tetrahydropyridino*-5′ : 6′-6 : 7-*dihydrocarbostyril*], m.p. 234—235°. R. S. C.

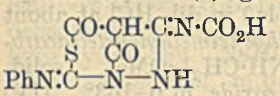

(IV.)

Formation of heterocyclic compounds from thioacetocarbamic acid derivatives. I. T. N. Ghosh (J. Indian Chem. Soc., 1936, **13**, 86—93).—Dicarbethoxythioacetocarbamic acid (I) (A., 1934, 400) and $NHPh \cdot NH_2$ (II) in EtOH give *Et* 3-*keto*-2-*phenyl*-2 : 3-*dihydro*-1 : 2 : 4-*triazolyl*-5-*malonate*, m.p. 203°, hydrolysed by 15% EtOH–KOH to the -5-*acetic acid*, m.p. > 300° (darkens at 280°), and thence by aq. 20% KOH to 3-*keto*-2-*phenyl*-5-*methyl*-2 : 3-*dihydro*-1 : 2 : 4-*triazole*, m.p. 210—212° (decomp.). (I) and N_2H_4,H_2O afford *Et* 3-*carboxylimino*-5-*pyrazolone*-4-*carboxylate* (+1·5H_2O), m.p. 181°, hydrolysed (10% EtOH–KOH) to 3-*carboxylimino*-5-*pyrazolone* (+2H_2O), m.p. > 300° (darkens at 250°) [4-*CHPh*: derivative (+2H_2O), resinifies slowly at > 280° (softens at 180°)], whilst acetylcarbethoxythioacetocarbamic acid (*loc. cit.*) and (II) give the *pyrazolone*,



$$NPh<\begin{matrix}NH \cdot C{:}N \cdot CO_2H \\ CO-CH \cdot CMe{:}N \cdot NHPh\end{matrix}$$

m.p. 185—186° (decomp.). Diacetylthioacetocarbamic acid (III) (*loc. cit.*) and N_2H_4,H_2O yield 3-*keto*-5-*diacetylmethyl*-, m.p. 70—71°, and thence (hydrolysis with 15% EtOH–KOH) 3-*keto-5-acetylmethyl-*, m.p. 228—230°, -2 : 3-*dihydro*-1 : 2 : 4-*triazole*. 4-Phenylthiosemicarbazide and (I) give the *thioheptadiazine* (IV), m.p. 183° (decomp.), which with Ac_2O affords PhNCS and tar; S is not removed from (IV) by yellow HgO. o-$C_6H_4(NH_2)_2$ and (I) in AcOH give *Et 2-benziminazolylmalonate*, m.p. 218°, hydrolysed (15% EtOH–KOH) to 2-methylbenziminazole; (III) similarly affords 2-*diacetylmethylbenziminazole*, m.p. 138—139° [*hydrochloride*, m.p. 243—244° (decomp.; turning green)], whilst (I) and $C_2H_4(NH_2)_2$ yield *Et* 4 : 5-*dihydro-2-glyoxalinylmalonate*, m.p. 100—101°. H. B.



(IV.)

Synthesis of glyoxaline derivatives from α-oximinoketones. 4-3′-Piperidylglyoxaline. E. Ochiai and S. Ikuma (Ber., 1936, 69, [*B*], 1147—1151).—Production of glyoxaline derivatives by reduction of oximinoketones (I) in presence of KCNS is not practicable, since the catalyst becomes poisoned, but addition of KCNS to the reduced solution of (I) effects the desired change. Thus OH·N:CAc·CO_2Et affords Et 2-thiol-4-methylglyoxaline-5-carboxylate, decomp. 229°, whilst CMeAc:N·OH gives 2-*thiol*-4 : 5-*dimethylglyoxaline*, m.p. about 270°. Replacement of CNS′ by CNO′ gives, respectively, Et 4-methylglyoxal-2-one-5-carboxylate, m.p. 220°, and 4 : 5-dimethylglyoxal-2-one, darkens at about 210°. Et oximinonicotoylacetate yields *Et* 2-*thiol*-4-3′-*pyridylglyoxaline-5-carboxylate* (II), decomp. 230—231° (*picrate*, decomp. 192°; *hydrochloride*, decomp. 116°). *Et 4-3′-pyridylglyoxal-2-one-5-carboxylate*, decomp. 258°, is described. (II) is converted by 3% H_2O_2 in presence of dil. H_2SO_4 at 40° into *Et 4-3′-pyridylglyoxaline-5-carboxylate*, m.p. 198°; the corresponding *acid*, decomp. 248°, is decarboxylated at 260° to 4-3′-*pyridylglyoxaline*, m.p. 40—41° (*hydrobromide*, decomp. > 320°), the *hydrochloride* of which is hydrogenated (Pt) under pressure to non-cryst. 4-3′-*piperidylglyoxaline*, b.p. 200—250° (bath)/0·001 mm. (*platinichloride*, decomp. > 330°; *monobenzoate*, m.p. 192°). H. W.

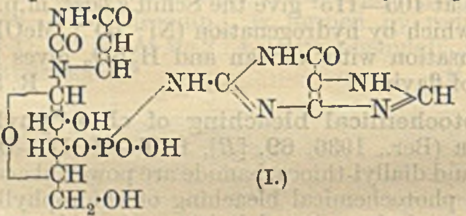
[Relation between] constitution and fluorescence of flavins. P. Karrer and H. Fritzsche (Helv. Chim. Acta, 1936, 19, 481—483).—8-Methyl- and 6 : 8-*dimethyl*-9-β-*hydroxyethyl*isoalloxazine (I) in H_2O or $COMe_2$ show brownish-yellow fluorescence in ultra-violet light, but none in daylight, and thus differ markedly from the alloxazines, although Me next to the N-ring has the same qual. effect in both series. Diazotisation of 5-nitro-*m*-4-xylidine at 0° and treatment with Cu first at room temp. and then at 100° gives 67·8% of 4-chloro-5-nitro-*m*-xylene, m.p. 51°, which with $NH_2·CH_2·CH_2·OH$ in hot C_5H_5N gives 5-*nitro*-N-β-*hydroxyethyl*-1 : 3 : 4-*xylidine*, m.p. 51°. Reduction with $Na_2S_2O_4$ in aq. EtOH, followed by reaction with alloxan, affords (I), m.p. 268° (uncorr.; decomp.) after sintering from 258°. R. S. C.

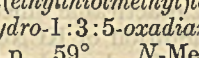
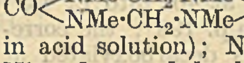
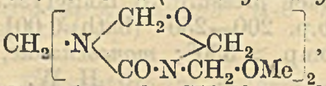
Syntheses in the flavin series. P. Karrer and F. M. Strong (Helv. Chim. Acta, 1936, 19, 483—493).—Attempts to synthesise flavins with 2 Me in positions other than 6 and 7 failed. 4-*Nitro*-N-*carbethoxy*-1 : 2 : 3-*xylidine* (prep. by $ClCO_2Et$ in $CHCl_3$), m.p. 115°, with H_2–Pt-black in EtOH gives 3-*carbethoxyamino*-1 : 2 : 4-*xylidine*, m.p. 127—129°, which by condensation with *l*-arabinose (I) in dry MeOH, followed by hydrogenation (Ni; 80°/25 atm.) gives 4-l-1′-*arabamino*-N-*carbethoxy*-1 : 2 : 3-*xylidine*, m.p. 182°. With 2·5*N*-KOH at 70° this gives nearly quantitatively 2-*hydroxy*-1-l-*arabityl*-4 : 5-*dimethylbenziminazole*, m.p. 247—248°. 5-Nitro-*m*-xylene (modified prep.) with H_2–PtO_2 in EtOH gives *s-m*-xylidine, b.p. 97—98°/12 mm., converted by conc. HNO_3–H_2SO_4 at 0—5° into 6- (II), m.p. about 45° (lit. 54°; converted by reduction and condensation with alloxan into a fluorescent solution of an alloxazine), and 4-*nitro*-s-m-*xylidine*, m.p. 136° (gives no alloxazine). The *CO_2Et*-derivative, m.p. 61·5°, of (II) is hydrogenated (PtO_2; EtOH) to 5-*carbethoxyamino*-1 : 3 : 4-*xylidine*, m.p. 116°, which gives only a trace of N-d-*ribityl* derivative, m.p. 164°, whence no flavin could be obtained. N-d-1′-*Arabityl*-1 : 3 : 4-*xylidine*, m.p. 145°, and PhN_2Cl give the *phenyldiazoamino*-compound, decomp. 150°. (I) and (II) in MeOH at 105—115° give the Schiff's *base*, m.p. 165—166°, which by hydrogenation (Ni; 60°; MeOH) and condensation with alloxan and H_3BO_3 gives only a trace of flavin. R. S. C.

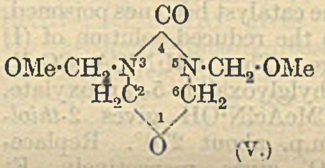
Photochemical bleaching of chlorophyll. K. Weber (Ber., 1936, 69, [*B*], 1026—1031).—Diethylallyl- and diallyl-thiocarbamide are powerful acceptors in the photochemical bleaching of chlorophyll (I) in presence of air; phenylallylthiocarbamide and allylthiosemicarbazide are about as efficient as thiosinamine, whereas hydrazine-*NN*′-dithiocarbonallylamide is less powerful. $FeSO_4$ is active in neutral or feebly acid solution. In absence of acceptor the rate of bleaching is slow; it increases rapidly in the presence of small amounts of acceptor, attains a max., and then diminishes approx. logarithmically with increasing acceptor concn. In all cases there is a marked induction period. The rate depends little on temp. Bleaching is greatly inhibited by quinol, toluquinol, *p*-benzoquinone, toluquinone, thymoquinone, p-$C_6H_4(OMe)_2$, PhOH, m-$C_6H_4(OH)_2$, o-$C_6H_4(OH)_2$, s-$C_6H_3(OH)_3$, thymol, p-$NO_2·C_6H_4·OH$, α-$C_{10}H_7·OH$, $NHPh_2$, NH_2Ph, and KI. Acceptors and inhibitors, except KI, do not extinguish fluorescence. The phenomena are explained by the hypothesis that the mol. of (I) activated by a light quantum brings the acceptor into an active state in which it combined with a mol. of O_2 giving a peroxide which then oxidises (I). Induction and photochemical after-effect are due to the long life-period of the intermediate peroxide. With high concn. of acceptor (I) is stabilised by the reaction $AO_2 + A \rightarrow 2AO$. H. W.

Magnetic properties and structure of hæmoglobin, oxyhæmoglobin, and carboxyhæmoglobin. L. Pauling and C. D. Coryell (Proc. Nat. Acad. Sci., 1936. 22, 210—216; cf. this vol., 616).—Magnetic measurements show that the two last-named contain no unpaired electrons; thus the O_2 mol., with two unpaired electrons, undergoes a profound change in electronic structure on attachment to hæmoglobin (I). The magnetic susceptibility of (I) corresponds with an effective magnetic moment of 5·46 Bohr magnetons per heme (Fe–porphyrin complex). This shows the presence of 4 unpaired electrons per heme, and indicates that the heme–heme interaction tends to stabilise the parallel configuration of the moments of the 4 hæms in the mol. The linkings from Fe to surrounding atoms are ionic in (I), and covalent in the other two compounds. N. M. B.

Nucleic acids. V. Hydrolytic fissions of yeast nucleic acid. H. Bredereck and G. Richter (Ber., 1936, 69, [*B*], 1129—1133).—Hydrolysis of yeast nucleic acid with boiling H_2O gives *guanine-uridylic acid* (I), $C_{14}H_{16}O_9N_7P$, the individuality of which is established by analysis, production essentially of guanine (II) when treated with HCl in MeOH, hydrolysis by 3·8% H_2SO_4 to guanine sulphate and uridylic acid (III) (isolated as the brucine salt) and by 3% NaOH to (II) and (III), and separation of (II) under the action of almond emulsin at p_H 4·9. The possibility of the presence of a mixture of (II) and (III) is excluded, since the material is relatively freely sol. in H_2O and the solution does not yield guanine picrate or brucine uridylate. Since (I) is monobasic acid (phenolphthalein) the union of (II) and (III) must occur through the PO_4 group. Further, since de-amination of (I) and subsequent hydrolysis with dil. H_2SO_4 affords (II) and (III), the NH_2 of (II) is not free, but linked to the PO_4 of (III). Hence (I) has the above constitution. Examination of the filtrate from (I) shows the presence of (II), adenine, (III), cytidylic acid, ribose, and H_3PO_4. H. W.


(I.)

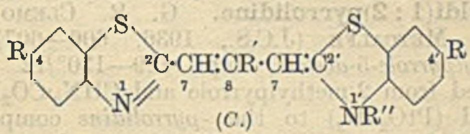
Carbamide–formaldehyde condensation products. H. Kadowaki (Bull. Chem. Soc. Japan, 1936, **11**, 248—261).—Many cryst. condensation products are isolated. CH_2O (1 mol.) and $CO(NH_2)_2$ (8 mols.) in dil. HCl under defined conditions give *methylenebiscarbamide* (I), $CH_2(NH\cdot CO\cdot NH_2)_2$, m.p. 218° (decomp.) (*$Ac_2$* derivative, m.p. 156°), which with a trace of HCl in H_2O gives *trimethylenetetra-*, m.p. 230° (decomp.), and *pentamethylenehexa-carbamide*, m.p. 236° (decomp.), $NH_2\cdot CO\cdot NH\cdot[CH_2\cdot NH\cdot CO\cdot NH]_x\cdot H$ (x=3 and 5, respectively). (I) and CH_2O with a trace of $Ba(OH)_2$ give, according to the conditions, ω-*hydroxymethyl-* ("*methylolmethylenedicarbamide*"), solid, and ωω′-*di*(*hydroxymethyl*)-*methylenebiscarbamide* ("*methylenebismethylolcarbamide*") (II), m.p. 228° (decomp.), $OH\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CH_2\cdot NH\cdot CO\cdot NHR$ (R=H and $\cdot CH_2\cdot OH$, respectively). Methylcarbamide, CH_2O, and HCl give similarly the ωω′-*Me_2* derivative, m.p. 184°, of (I) ("*methylenebismethylcarbamide*"). *N*-Hydroxymethylcarbamide ("methylolcarbamide") (III) with MeOH or EtOH and a trace of HCl gives the *Me*, m.p. 91°, and *Et ether*, m.p. 111°. *NN′*-Di(hydroxymethyl)carbamide ("dimethylolcarbamide") (IV) gives similarly the *Me_2*, m.p. 101°, *Et_2*, m.p. 124°, *$Pr^a{}_2$*, m.p. 95°, *$Bu^a{}_2$*, m.p. 93°, *di*-n-*amyl*, m.p. 84°, and *dibenzyl ether*, m.p. 112°, and with SHEt and a little HCl *NN′*-*di*(*ethylthiolmethyl*)*carbamide*, m.p. 108·5°. (II) gives similarly the *Me_2 ether*, m.p. 240° (decomp.). CH_2O (1 mol.) and carbamide (8 mols.) in dil. HCl at about —5° give ωω′-*di*(*methoxymethyl*)*trimethylenetetracarbamide*, $OMe\cdot CH_2\cdot[NH\cdot CO\cdot NH\cdot CH_2]_4\cdot OMe$, solid. (III) and acid H_2O_2 give a *peroxide*, m.p. 163°. (IV) with neutral H_2O_2 gives a liquid *peroxide*, with H_2O_2 and acid a cryst. *peroxide*, but with slightly acid H_2O_2 a polymeric, amorphous *peroxide*, $CO(NH\cdot CH_2\cdot O_2\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CH_2\cdot O_2H)_2$. When CH_2O (4 mols.) and carbamide (1 mol.) are condensed in aq. $Ba(OH)_2$ and then treated with MeOH and HCl, there is obtained 3 : 5-*di*(*methoxymethyl*)*urone* [4-*keto*-3 : 5-*di*(*methoxymethyl*)*tetrahydro*-1 : 3 : 5-*oxadiazine*] (V), b.p. 82—83°/0·1 mm. (the hypothetical 4-keto-tetrahydro-1 : 3 : 5-oxadiazine,  $O\left<\begin{matrix}CH_2\cdot NH\\CH_2\cdot NH\end{matrix}\right>CO$, is termed "urone"), which with SHEt and a little HCl gives 3 : 5-*di*(*ethylthiolmethyl*)*urone* [4-*keto*-3 : 5-*di*(*ethylthiolmethyl*)*tetrahydro*-1 : 3 : 5-*oxadiazine*], m.p. 59°. *N*-Methyl- and -ethyl-carbamide lead similarly to 3-*methyl*-5-*methoxymethyl*-, b.p. 89—90°/0·2 mm., and -5-*ethylthiolmethyl*-, b.p. 122—125°/1 mm., 3-*ethyl*-5-*methoxymethyl*-, b.p. 91—93°/1 mm., and -5-*ethylthiomethyl-urone*, m.p. 15·5°, b.p. 110—113°/1 mm. [4-*keto*-3-*methyl*-5-*methoxymethyltetrahydro*-1 : 3 : 5-*oxadiazine* etc.]; $CO(NHMe)_2$ gives 3 : 5-*dimethylurone* [4-*keto*-3 : 5-*dimethyltetrahydro*-1 : 3 : 5-*oxadiazine*], m.p. 38·5°, and *tetramethyldimethylenediureide*,  $CO\left<\begin{matrix}NMe\cdot CH_2\cdot NMe\\NMe\cdot CH_2\cdot NMe\end{matrix}\right>CO$, m.p. 258° (also obtained in acid solution); $NH_2\cdot CO\cdot NMe_2$ gives NN-*dimethyl*-N′-*methoxymethylcarbamide*, m.p. 65°; (I) gives 3 : 3′-*methylenebis*-5 : 5′-*dimethoxymethylurone* [-*bis*-4-*keto*-5 : 5′-*di*(*methoxytetrahydro*-1 : 3 : 5-*oxadiazine*)],  $CH_2\left[\cdot N\left<\begin{matrix}CH_2\cdot O\\ \\CO\cdot N\cdot CH_2\cdot OMe\end{matrix}\right>CH_2\right]_2$, a gum. (II), its Bu_2, diamyl, and $(CH_2Ph)_2$ ethers, when heated, give transparent resins with great resistance to H_2O. 20 photomicrographs are given. R. S. C.


(V.)

Thiazolinephenols. Synthesis and proof of structure. J. B. Niederl, W. F. Hart, and J. V. Scudi (J. Amer. Chem. Soc., 1936, 58, 707—708)—Allylthiocarbimide (0·5 mol.), PhOH (1 mol.), and conc. H_2SO_4 (1 mol.) at 0—5° (24 hr.) and then at room temp. (3 days) give 2-p-*hydroxyphenyl*-5-*methylthiazoline*, m.p. 166—168° (*hydrochloride*, m.p. 187°; *picrate*, m.p. 178°), oxidised ($KClO_3$, dil. HCl) to *p*-$OH\cdot C_6H_4\cdot CO_2H$ and $NH_2\cdot CH_2\cdot CHMe\cdot SO_3H$. 2-4′-*Hydroxy*-2′-*methylphenyl*-, m.p. 131° (*hydrochloride*, m.p. 175°; *picrate*, m.p. 154°), 2-4′-*hydroxy*-3′-*methoxyphenyl*-, m.p. 142° (*hydrochloride*, m.p. 187°; *picrate*, m.p. 159—160°), and 2-2′ : 4′-*dihydroxyphenyl*-, m.p. 184° (*hydrochloride*, m.p. 251°; *picrate*, m.p. 190°), -5-*methylthiazolines* are similarly prepared from *m*-cresol, guaiacol, and *m*-$C_6H_4(OH)_2$, respectively. H. B.

Thiazoles. XXII. Synthesis of some 6-methoxy- and 5 : 6-dimethoxy-benzthiazoles and of certain dyes obtainable therefrom. M. G. Ast and M. T. Bogert (Rec. trav. chim., 1935, **54**, 917—930).—*p*-OMe·C_6H_4·NH_2,HCl and S_2Cl_2 give a condensation *product*, m.p. 168—168·5° (corr.) (decomp.), hydrolysed by $NaHCO_3$–$Na_2S_2O_4$ to 2-*amino*-5-*methoxythiophenol*, m.p. 110° [*Na* and *Zn* (I) salt; Bz_2 derivative, m.p. 162—162·5° (corr.), yields 1-phenyl-5-methoxybenzthiazole, m.p. 114—114·5° (cf. lit.)]. (I) with AcOH and *p*-NO_2·C_6H_4·COCl (II) gives 1-p-*nitrophenyl-5-methoxybenzthiazole* (III), m.p. 215—216·5° (corr.). The corresponding m-NO_2-compound, m.p. 161·5—162·5° (corr.), similarly prepared, was obtained together with a trace of 1-m-*nitrophenyl-5-methoxychlorobenzthiazole*, m.p. 199·5—200·5° (corr.). (I) and *o*-NO_2·C_6H_4·CHO give a *compound*, m.p. 123·5—124·5° (corr.), reduced by $SnCl_2$ to a *compound*, m.p. 108·5—109·5° (corr.); these were not investigated further. (III) when refluxed with $SnCl_2$–AcOH–HCl yields 1-p-*aminophenyl-5-methoxybenzthiazole*, m.p. 195—196° [corresponding m-NH_2-derivative, m.p. 128·5—129·5° (corr.)]. (I) with *p*-NMe_2·C_6H_4·CHO–AcOH affords 1-p-*dimethylaminophenyl-5-methoxybenzthiazole* (III), m.p. 181·5—182·5° (corr.). 6 : 6′-Dinitro-3 : 4 : 3′ : 4′-tetramethoxydiphenyl disulphide (V), m.p. 232—232·5° (corr.) (cf. lit.), prepared from 4 : 5-dinitroveratrole, Na_2S, S, and MeOH, when treated with Zn–AcOH gives a solution of *Zn 2-amino-4 : 5-dimethoxyphenyl mercaptide* (VI), which with (II) gives an amorphous *product* (VII), m.p. 238·5—239·5° (corr.), reduced by $SnCl_2$–HCl–AcOH to 1-p-*amino*-4 : 5-*dimethoxybenzthiazole*, m.p. 224·5—225·5° (corr.) [the corresponding o-, m.p. 196·5—197·5° (corr.), and m-*amino*-compound, m.p. 206—206·5° (corr.)]. (VI) and (II) with anhyd. NaOAc gives a cryst. product, which on heating to 190—195° or attempted crystallisation is converted into (VII). (V) when boiled with $Na_2S_2O_4$, NaOH, and H_2O and then treated with BzCl at room temp. gives *dibenzoyl*-2-*amino*-4 : 5-*dimethoxythiophenol*, m.p. 149·5—150° (corr.), converted by hot AcOH–NaOAc into 1-*phenyl*-4 : 5-*dimethoxybenzthiazole*, m.p. 149—150°; 1-o-, m.p. 162—163·5° (corr.), and 1-m-, m.p. 186—187° (corr.), -*nitrophenyl*-4 : 5-*dimethoxybenzthiazole* were similarly prepared. (VI) and *p*-NMe_2·C_6H_4·CHO give 1-p-*dimethylaminophenyl*-4 : 5-*dimethoxybenzthiazole*, m.p. 231—232°. This and (IV) when methylated yield 1-p-*dimethylamino*-4 : 5-*dimethoxy*-, m.p. 221—224° (corr.), and -5-*methoxy*-, m.p. 217·5—218·5° (corr.), -*benzthiazole methiodide*, respectively, which are thioflavine dyes, unstable to light or washing. *Chloramine-yellows* were obtained by treating the aminobenzthiazoles described with H_2SO_4–SO_3 and the resulting sulphonic acid with NaOCl. The tinctorial properties of the dyes are described. H. G. M.

Cyanine dyes. VIII. Synthesis of 8-methyltrimethinethiocyanine derivatives and the reactivity of the 8-methyl group. T. Ogata (Bull. Chem. Soc. Japan, 1936, **11**, 262—264).—The following are prepared from the appropriate 2-methylbenzthiazole ethiodide and Ac_2O–HCO_2K (*A*) or Ac_2O–KOAc (*B*) at 150—165°, the data in parentheses being, respectively, method, yield, and sensitisation max. in mμ: 1 : 1′-diethyl- (A., 1934, 422) (*A*), 1 : 1′-*diethyl*-8-*methyl*- (*B*, 30%), m.p. 286° (decomp.) (580), 1 : 1′ : 4 : 4′ : 8-*pentamethyl*- (*B*, 20%), m.p. 279° (decomp.) (580), and 8-*methyl*-1 : 1′-*diethyl*-3 : 4 : 3′ : 4′-*dibenzo*- (*B*, 70%), m.p. 293° (decomp.) (600), -*trimethinethiazolocyanine iodide* [all as (*C*)]. The 8-Me derivatives condense with aldehydes and piperidine to give the corresponding 8-β-substituted vinyl compound, and thus are obtained: 1 : 1′-*diethyl*-8-β-*furylvinyl*-, m.p. 277° (decomp.) (*C*, R′=CH:CH·C_4H_3O), -8-*styryl*- (R′=CH:CHPh), m.p. 266° (decomp.) (600), and -8-p-*dimethylaminostyryl*-, m.p. 252° (decomp.) (600), -*trimethinethiazolocyanine iodide*; 1 : 1′-*diethyl*-8-*styryl*-, m.p. 265° (decomp.), and -8-p-*dimethylaminostyryl*-, m.p. 288°, -3 : 4 : 3′ : 4′-*dibenzotrimethinethiazolocyanine iodide*, and 1 : 1′ : 4 : 4′-*tetramethyl*-8-p-*dimethylaminostyryltrimethinethiazolocyanine iodide*, m.p. 292° (decomp.). J. W. B.



(*C*.)

Alkaloids of *Heliotropium lasiocarpum*. V. Lasiocarpine. G. Menschikov and J. Schdanovitsch (Ber., 1936, **69**, [*B*], 1110—1113; cf. A., 1932, 865).—Lasiocarpine (I) is hydrolysed by boiling 2% NaOH to heliotridine and angelic acid. Hydrogenation (PtO_2 in 0·5*N*-HCl) of (I) affords *lasiocarpic acid*, $C_8H_{16}O_5$, m.p. 95—97°, $[\alpha]_D$ +10·6° in EtOH, which contains 2 OH (Zerevitinov) and 1 OMe, and a non-cryst. *base*, $C_{13}H_{23}O_2N$, b.p. 123—125°/8 mm., $[\alpha]_D$ +3·8° in EtOH (*picrate*, m.p. 157—159°), hydrolysed by KOH–EtOH to hydroxyheliotridane and CHMeEt·CO_2H. H. W.

Electrolytic reduction of vasicine. K. S. Narang and J. N. Ray (J.C.S., 1936, 686—688).—In reply to Späth and Platzer (this vol., 489), the reduction of *B* (cf. A., 1935, 765) for 5 hr. gives a *base*, $C_{11}H_{12}ON_2$, m.p. 115°, whilst similar reduction of vasicine (I) gives a *base*, $C_{11}H_{14}ON_2$ [*picrolonate*, m.p. 165—168° (decomp.)], the first addition of H taking place at N:C in the middle ring. Reduction of (I) for a longer period yields a *base*, $C_{11}H_{12}N_2$, m.p. 92° [*picrolonate*, m.p. 224—228° (decomp.)]. The constitution of the various reduction products of (I) is discussed, and the structure assigned previously to (I) is confirmed. F. R. S.

Identity of tazettine from *Narcissus Tazetta*, L., with "base VIII," from *Lycoris radiata*, Herb. E. Späth, H. Kondo, and F. Kuffner (Ber., 1936, **69**, [*B*], 1086—1087).—Tazettine is identical with Kondo's "base VIII" (J. Pharm. Soc. Japan, 1932, **52**, 51) which is therefore, $C_{18}H_{21}O_5N$; it has $[\alpha]_D^{18}$ +165·1° in $CHCl_3$. Their identity with ungernine (Norkina *et al.*, this vol., 618) is probable. H. W.

Tobacco alkaloids. VII. New synthesis of *dl*-anabasine. E. Späth and L. Mameli (Ber., 1936, **69**, [*B*], 1082—1085).—1-Benzoylpiperidone, m.p. 110—112°, from piperidone and Bz_2O at 180°, is condensed with Et nicotinate by NaOEt in C_6H_6 at 110—115° to *anabaseine*, $C_{10}H_{12}N_2$, b.p. 110—120°

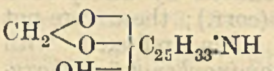
(bath)/1 mm. [*dipicrate*, m.p. 174° (vac.; slight decomp.)], which is reduced (Pd–C in 3·% AcOH) to *dl*-anabasine, identical with that obtained by racemisation of the natural base. The *dipicrolonate* has m.p. 258—259°. H. W.

Lupin alkaloids. IX. Synthesis of 5 : 5′-dimethyldi(1 : 2)pyrrolidine. G. R. CLEMO and T. P. METCALFE (J.C.S., 1936, 606—607).—*Et 2-methylpyrrole-5-acetate*, b.p. 129—130°/12 mm., obtained from 2-methylpyrrole and $CHN_2·CO_2Et$, is reduced (PtO_2–H_2) to the *-pyrrolidine* compound, b.p. 98°/12 mm. (*picrate*, m.p. 112°; *picrolonate*, m.p. 194°), which condenses with $CHMeBr·CO_2Et$ to *Et 2-methylpyrrolidine-5-acetate*-1-*α-propionate*, b.p. 150—151°/12 mm. This ester with K forms 4-*keto*-5 : 5′-*dimethyldi*(1 : 2)*pyrrolidine*, b.p. 65°/1 mm. (*picrate*, m.p. 186°; *picrolonate*, m.p. 217°), which is reduced (Zn–HCl) to the 4-*hydroxy*-compound, b.p. 68—70°/1 mm. (*picrolonate*, m.p. 205°) but with N_2H_4 affords 5 : 5′-*dimethyldi*(1 : 2)*pyrrolidine*, b.p. 25°/1 mm. (*picrate*, m.p. 249°; *picrolonate*, m.p. 180°). F. R. S.

Hydrobromoquinine. J. K. PODLEWSKI and J. SUSZKO (Rec. trav. chim., 1936, **55**, 392—400; cf. this vol., 490).—Quinine hydrochloride with 38% HBr–AcOH at 80° affords a partly racemised mixture of *hydrobromoquinine dihydrobromide* (*A*), m.p. 223—225° (decomp.), $[\alpha]_D^{20}$ −140° to −150° in H_2O (*dinitrate*, decomp. 180—210°, $[\alpha]_D^{20}$ −150° to −170° in H_2O). With 48% aq. HBr–10% $NaNO_2$ or 10% NaOAc (*A*) gives the *monohydrobromide*, m.p. 200—210° (decomp.). Crystallisation from C_6H_6 of the bases liberated by the action of aq. NH_3 on (*A*) affords plates of $C_{20}H_{25}O_2N_2Br$, $+C_6H_6$, m.p. 105°, resolidifying and decomp. at 140°, $[\alpha]_D^{20}$ −130° to −150°, and needles, decomp. 140°, $[\alpha]_D^{20}$ −115° to −140°, of the solvent-free base. Both cryst. forms give a mixture of β-*iso*quinine and niquine when hydrolysed with KOH–EtOH. Separation of the stereoisomerides is effected by fractional crystallisation of the Et_2O extract of (*A*) basified with 10% NaOH, which affords *hydrobromoquinine*-II, m.p. 166—167° (decomp.), $[\alpha]_D^{20}$ −200° in EtOH–$CHCl_3$ [*metho*-p-*toluenesulphonate*, m.p. 145—155° (decomp.), $[\alpha]_D^{20}$ −114° in EtOH, and CH_2PhBr additive *salt*, m.p. 185—190° (decomp.), $[\alpha]_D^{20}$ −142° in EtOH], and, from the Et_2O mother-liquor, *hydrobromoquinine*-I, solvent-free, m.p. 160—162° (decomp.), $[\alpha]_D^{20}$ −182° to −186°, and $+C_6H_6$, $[\alpha]_D^{20}$ −50° in EtOH–$CHCl_3$ [*metho*-p-*toluenesulphonate*, $+H_2O$ and anhyd., m.p. 193—194° (decomp.), $[\alpha]_D^{20}$ −59° in EtOH, and CH_2PhBr additive *salt*, m.p. 185—190° (decomp.), $[\alpha]_D^{20}$ −95° in EtOH]. When heated with 3% KOH–EtOH, base-I gives only β-*iso*quinine, and base-II gives only niquine. Base-I and -II are stereoisomeric *tert*. bases. J. W. B.

Alkaloids of white hellebore. II. Isolation of alkaloids from the so-called resinous matters. K. SAITO and H. SUGINOME. **III. Constitution of jervine.** K. SAITO and M. TAKAOKA (Bull. Chem. Soc. Japan, 1936, **11**, 168—171, 172—176).—II. Extraction of the resin remaining after EtOH-extraction of the roots (A., 1934, 422) with dil. AcOH affords a sol. portion from which jervine (I) is isolated, and an insol. portion (2·5% of roots). Prolonged Et_2O-extraction of the latter removes 18%, from which ligroin (b.p. 40—60°) dissolves 19% of fats leaving an insol. *substance*, m.p. 262° (decomp.). From the Et_2O-insol. residue are isolated phenolic substances, sol. acids including angelic and an *acid*, m.p. 102°, and alkaloids from which more (I) (total yield 0·6% of roots) is obtained.

III. Pure (I), m.p. 243·5—244·5° (bath preheated to 180°), $[\alpha]_D^{21}$ −150° in EtOH, with CH_2N_2 or MeI–KOH–EtOH gives its N-*Me* derivative, $+H_2O$ and anhyd., m.p. 201—202° [*methiodide*, m.p. about 247°, by MeI at 100°; *methochloride*, m.p. 252° (decomp.); *Ac* derivative, m.p. 186—187°], and with $NaNO_2$–AcOH a *NO*-derivative, m.p. 251—252° (decomp.). (I) with Ac_2O at room temp. affords its N-*Ac* derivative, $+H_2O$ and anhyd. (II), m.p. 161—162° (decomp.), and with boiling Ac_2O an ON-*Ac_2* derivative, m.p. 176—177°, hydrolysed by 0·1*N*-NaOH–EtOH to (II). In agreement with these data (I) contains 2 active H (Zerevitinov) and is represented by the partial formula (*A*). J. W. B.



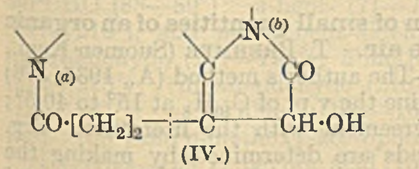
$$\left.\begin{matrix}\mathrm{CH_2}{<}\begin{matrix}\mathrm{O}-\\\mathrm{O}-\end{matrix}\\\mathrm{OH}-\end{matrix}\right\}\mathrm{C_{25}H_{33}{:}NH}$$

(*A*.)

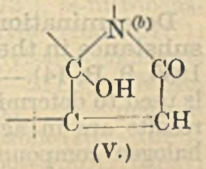
Alkaloids of *Holarrhena antidysenterica*. IV. Occurrence of two further new bases in the bark of Indian *Holarrhena* and their relationship to conessine and holarrhimine. S. SIDDIQUI. **V. Holarrhimine.** S. SIDDIQUI and R. H. SIDDIQUI (Proc. Indian Acad. Sci., 1936, **3**, A, 249—266; 257—260).—IV. From the mother-liquor of holarrhimine sulphate (A., 1933, 289) are isolated (insolubility of their hydrochlorides in 10% HCl and fractional crystallisation from ligroin) *conamine* (I), $C_{22}H_{36}N_2$, probably $C_{21}H_{31}(NMe)·NH_2$, m.p. 130°, $[\alpha]_D^{28}$ −19° in EtOH, converted by heating to dryness into a *substance*, m.p. 220—240°, and *conarrhimine* (II), (?) $C_{21}H_{31}(NH)·NH_2$. The latter was not obtained pure since it forms eutectic mixtures, of sharp m.p. 160° and m.p. 175°, with holarrhimine (III), into which they are converted completely by heating with moist EtOAc. These observations may explain the isolation of kurchicine (Ghosh *et al.*, A., 1928, 1265). The presence of (II) was established by the isolation of *nitrosohydroxy*apo*conarrhimine*, $C_{21}H_{31}(N·NO)·OH$, sinters 145°, m.p. 160—163° [together with $C_{21}H_{31}(OH){:}NMe$ from (I) and $C_{21}H_{31}(OH)_3$ from (III)], by the action of HNO_2 on the mother-liquor from (I). Contrary to earlier statements (*loc. cit.*) (III) contains 5 active H atoms, $C_{21}H_{31}(NH_2)_2(OH)$, and is converted by 40% CH_2O–HCO_2H into *tetra*-N-*methylholarrhimine*, m.p. 233—235°, $[\alpha]_D^{33}$ −45·5° in EtOH (also obtained by direct methylation of the total bases from *Holarrhena* bark) {*hydrochloride*, m.p. 315—316° (decomp.); *hydriodide*, m.p. 302—303° (decomp.); *hydrobromide*, m.p. 306—307°; *picrate*, sinters 225°, m.p. 272—275°; *platinichloride*, m.p. 251—252°; *monomethiodide*, m.p. 286—287° (decomp.); *Bz*, m.p. 176° [*hydrochloride*, shrinks 163°, m.p. 237—238° (decomp.); *picrate*, evolves H_2O at 105—160°, decomp. 205—210°], and *Ac* derivative, softens 134°, m.p. 139—140° [*hydrochloride*, decomp. 230—273°; *picrate*, evolves H_2O at 105°, m.p. 160°, decomp. 202—205°]}. (II) is probably the parent of the alkaloid constituents of *H. antidysenterica.*

V. With BzCl (4 mols.)–C_5H_5N (III) gives a Bz_3 derivative, m.p. 269—270°, and, from the mother-liquor, a Bz_2 derivative, decomp. 115°, and with Ac_2O–NaOAc, a Ac_3 derivative, $+H_2O$ and anhyd., m.p. 249—250°. (III) contains 1 double linking and with Br–$CHCl_3$ a *dibromide*, m.p. 290—295° [m.p. 226—228° (decomp.) after liberation from its solution in AcOH by NaOH], is obtained. With MeI–$CHCl_3$ (III) gives a *dimethiodide*, m.p. 279°, converted (loss of HI and MeOH) by aq. NH_3, NaOH, or AgOH into *methylholarrhimine*, m.p. 170° [*hydrochloride*, m.p. 266° (decomp.); *platinichloride*, m.p. 245° (decomp.); *picrate*, m.p. 205°]. J. W. B.

Structure of strychnine. III. Strychninolone and its derivatives. M. Kotake and T. Mitsuwa (Bull. Chem. Soc. Japan, 1936, **11**, 231—238).—Oxidation of strychnine ($KMnO_4$–$COMe_2$) affords *dihydroxystrychnine*, +MeOH, $+2{\cdot}5H_2O$, and solvent-free, decomp. 100°, resolidifies, shrinks at 155°, m.p. 240° (*hydrochloride*, decomp. 212°; *methiodide*, m.p. 322°). Fractional crystallisation of Leuchs' strychninolone-*a* (I), m.p. 228—230°, from MeOH separates it into *strychninolone*-α (II), m.p. 224° (*Ac* derivative, m.p. 240—243°), and -β, m.p. 240° (less sol.) (*Ac* derivative, m.p. 253°), both $C_{19}H_{18}O_3N_2$ (different positions of double linking) and both reduced by Pd–H_2 to the same H_2-derivative m.p. 274°. (II) with 10% KOH gives isomeric *strychninolone*-γ (III), m.p. 254° (*Ac* derivative, m.p. 260°), which gives a different H_2-derivative, and is probably formed by OH-migration. (I) with NaOEt–EtOH gives *strychninolone*-δ (IV), $+3H_2O$, and anhyd., m.p. 285—286° (decomp.) (*Ac* derivative, $+H_2O$, m.p. > 340°; not reduced by Pd–H_2), and (I) with NH_3–MeOH gives, by fractional crystallisation of the product from H_2O, (III) and *strychninolone*-ε (V), $+H_2O$ and anhyd., m.p. 240—243° (*Ac* derivative, m.p. 214—215°; H_2-derivative, m.p. 257°). Oxidation of (I) with CrO_3–AcOH gives *strychninone*, m.p. 273° (yellow solution in alkali, repptd. by CO_2), and dihydrostrychninolone-α similarly gives *dihydrostrychninone*, m.p. 314° (colourless solution in alkali, not repptd. by CO_2). The structural implications of these results are discussed, the partial formulæ above being suggested. J. W. B.



(IV.)



(V.)

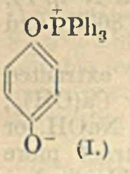
Iodo-derivatives of brucine. G. Sollazzo (Boll. Chim. farm., 1936, **75**, 213—219).—The compounds $C_{23}H_{27}O_4N_2I_3$, new m.p. 239—241°, and $C_{23}H_{27}O_4N_2I_4$, and the *compound* $C_{23}H_{27}O_4N_2I_3,3H_2O$, are prepared from brucine and I in EtOH under varying conditions. E. W. W.

Organic compounds of germanium. K. Burschkies (Ber., 1936, **69**, [*B*], 1143—1146).—*Sulphides*, $S(GeR_3)_2$, are obtained by heating the appropriate bromide with Na_2S alone or in EtOH; R=*Ph*, m.p. 138°; *tolyl*, m.p. 156—157°; CH_2Ph, m.p. 124°; C_6H_4Ph, m.p. 238°, cyclo*hexyl*, m.p. 87—88°; *Et*, b.p. 148—150°/12 mm. They are well-cryst. compounds with sharp m.p. and completely insol. in alkali. *Ge tetra*-β-*phenylethyl*, m.p. 56—57°, is obtained from $CH_2Ph{\cdot}CH_2{\cdot}MgBr$ and $GeCl_4$ in Et_2O. $Ge(CH_2Ph)_4$ is unattacked by HNO_3 (*d* 1·52) in AcOH at 15—20° or 50—60° and decomposed at the b.p. into Ge and $NO_2{\cdot}C_6H_4{\cdot}CHO$. Di-*p*-dimethylaminophenylgermanic anhydride is transformed by HNO_3 (*d* 1·52)–conc. H_2SO_4 at room temp. into the 3-NO_2-derivative. Tolylgermanic anhydride is oxidised by $KMnO_4$ in boiling H_2O to *di*-p-*carboxyphenylgermanic anhydride*. H. W.

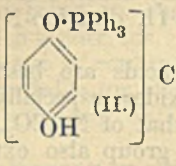
Mercury acetamide as a mercurating agent. II. Mercuration of phenols. K. G. Naik and B. V. Merta (J. Indian Chem. Soc., 1935, **12**, 783—787).—Hg acetamide when heated with the appropriate phenol in EtOH gives rise to OH·Hg-derivatives, the constitution of which was established by conversion by means of Br into the corresponding Br-derivatives. The following have been prepared: 2-*nitro*-4-*hydroxymercuriphenol*, m.p. > 285°, unaffected by dil. HCl, KI, H_2S, or $(NH_4)_2S$, but when heated with conc. HCl gives *o*-$NO_2{\cdot}C_6H_4{\cdot}OH$; 4-*nitro*-2-*hydroxymercuriphenol*, m.p. > 285°, converted by hot AcOH into 4-*nitro*-2-*acetoxymercuriphenol*, m.p. > 285°, which with $Na_2S_2O_3$–H_2O gives 2 : 2′-*mercuribis*-4-*nitrophenol*, m.p. > 285°; 1-*hydroxymercuri*-β-*naphthol* (I), m.p. 210° (decomp.), which with hot dil. HCl gives β-$C_{10}H_7{\cdot}OH$, with H_2S–H_2O gives HgS, and with KI gives 2KOH quantitatively, and is converted by hot AcOH into 1-*acetoxymercuri*-β-*naphthol*, m.p. 185°; 4-*hydroxymercuri*-α-*naphthol*, m.p. > 285°; *trihydroxymercuriphloroglucinol*, m.p. > 285°. (I) with dil. NaOH and CS_2 gives 1-*thiolmercuri*-β-*naphthol*, m.p. > 285°; o-, m.p. > 285°, and p-*thiolmercuriphenol* were similarly prepared from the appropriate chloromercuriphenol. H. G. M.

Manufacture of heterocyclic mercury compounds.—See B., 1936, 572.

Quinonephosphines. I. Benzoquinone-triphenylphosphine. A. Schönberg and R. Michaelis (Ber., 1936, **69**, [*B*], 1080—1082).—*p*-Benzoquinone and PPh_3 in C_6H_6 afford p-*benzoquinone-triphenylphosphine* (I) decomp. > 270°, hydrolysed by boiling 50% KOH to PPh_3O and quinol. (I) is converted by boiling 2*N*-HCl into the *hydrochloride* (II), decomp. (indef.) 290—300°, and by EtI in EtOH into the *ethiodide* [(II) with OEt for OH and I for Cl], m.p. about 235° (decomp.). H. W.



(I.)



(II.)

Synthesis of selenophen derivatives. I. Action of chlorine and bromine on selenophen. H. Suginome and S. Umezawa (Bull. Chem. Soc. Japan, 1936, **11**, 157—167).—Selenophen (I) with Cl_2 at 50—60° gives its 2-*Cl*-, b.p. 42°/12·5 mm., and 2 : 5-Cl_2- (II) -derivative, b.p. 67°/12 mm., and (best with excess of Cl_2) 2 : 2 : 3 : 4 : 5 : 5-*hexachlorotetrahydroselenophen*, m.p. 55°, oxidised by fuming HNO_3

at —21° to 15° to its 1-*oxide*, m.p. 172—172·5° (decomp.). (I) with Cl_2–CS_2 at —15° gives 2 : 3 : 4 : 5-*tetrachlorotetrahydroselenophen*, m.p. 97° (decomp.), decomposed at 95° to (II) and 2 : 2 : 5 : 5-*tetrachlorotetrahydroselenophen*, m.p. 96—98° [oxidised to its 1-*oxide*, m.p. 149—150° (decomp.)]. (I) with 20% Br–CS_2 at —15° gives the 1 : 1-*dibromide* (III), m.p. 152° (decomp.), of 2 : 2 : 5 : 5-*tetrabromotetrahydroselenophen* (IV), m.p. 97°, which is obtained, together with its 1-*oxide* (V), m.p. 128·5—130° (decomp.), by decomp. with H_2O, and is reconverted into (III) by Br–CS_2 at room temp. (V) is also obtained by oxidation of (IV) with fuming HNO_3, and is reconverted into (IV) by either hot *cyclo*hexanol or hot PhMe. A 10% solution of (I) in CS_2 with cold 10% Br–CS_2 gives 2-*bromoselenophen*, b.p. 59°/13 mm., the 2 : 5-*Br_2*- (VI), b.p. 42°/0·02 mm., and 2 : 3 : 5-*Br_3*-derivative, b.p. 94°/0·12 mm., m.p. 38°, being obtained when excess of Br is used. Excess of Br and (I) without solvent give *tetrabromoselenophen*, m.p. 102°, oxidised by fuming HNO_3 to $(\dot{:}CBr\cdot CO_2H)_2$. Excess of Cl_2 and a CS_2 solution of (VI) give 2 : 5-*dibromo*-2 : 3 : 4 : 5-*tetrachlorotetrahydroselenophen*, m.p. 70—72°. J. W. B.

Preparation of dibenzanthronyl, mixed benzanthrone–anthraquinone, dianthraquinonyl, and benzanthrone selenoethers.—See B., 1936, 489.

X-Ray studies of protein structure. W. T. Astbury (Nature, 1936, **137**, 803—805).—A summary of three lectures. L. S. T.

Nature of ostacin-ovo-ester from lobsters. P. Karrer and H. Hübner (Helv. Chim. Acta, 1936, **19**, 479—480).—In spite of its hypophasic behaviour on partition, the ostacin ester from lobster eggs ("ovo-ester") (prep. detailed) is shown by analysis to be $C_{40}H_{47}O_4\cdot CO\cdot C_{5-7}H_{11-15}$ or an ester of a similar, but unsaturated, acid. R. S. C.

Separation of amino-acids. III. Adsorption of amino-acids by Japanese clay from protein hydrolysate. IV. Dissolving out of amino-acids adsorbed by Japanese clay. M. Mashino and N. Shikazono (J. Soc. Chem. Ind. Japan, 1936, **39**, 88B).—III. Of the various forms of N in the hydrolysate of soya-bean protein after removal of glutamic acid, Japanese clay adsorbs total N 45·14, NH_3-N 21·77, humin-N 63·11, diamino-N 86·21, and monoamino-N 20·16%.

IV. The adsorbed NH_2-acids are best extracted with alkaline-earth hydroxides, especially $Ca(OH)_2$; its dissolving power is < that of Na_2CO_3, NaOH, or aq. NH_3, but the latter group also extract more colouring matter and render the clay colloidal, unless $Ca(OH)_2$ or EtOH is also added. J. W. B.

Constituents of acid globulins. Protein-*C*.—See this vol., 875.

Apparatus for drying organic compounds decomposed by heat. J. Bouillot (J. Pharm. Chim., 1936, [viii], 23, 605—607).—Apparatus for drying under reduced pressure at 30—60° is described. J. L. D.

Ashing of organic matter with nitric acid. H. Kaunitz (Mikrochem., 1936, 20, 104—106).—Vessels are described for avoiding loss of material by spurting during ashing with HNO_3, which can be done in 3 hr. J. W. S.

Pregl's absorption apparatus for micro-determination of carbon and hydrogen.—See this vol., 815.

Structure in relation to chromic oxidation of nitrogenous substances. C. N. Acharya (Biochem. J., 1936, 30, 1026—1032; cf. this vol. 352).—In the determination of N by the K_2CrO_4–H_2SO_4 oxidation method with substances containing C–2N and C–3N linkings and NH_2OH derivatives the low vals. obtained are due to the formation of N_2O; with N_2H_4 and azo-derivatives, to the formation of N_2. The method is modified by collecting the gases evolved after absorption of CO_2 and determining the O_2 by pyrogallol absorption and the N_2O by explosion with H_2. H. D.

Determination of nitrogen by the Kjeldahl method.—See this vol., 811.

Micro-analytical determination of active hydrogen by the Tschugaev and Zerevitinov method. Simultaneous determination of the active hydrogen atom and of the Grignard reagent consumed. A. Soltys (Mikrochem., 1936, 20, 107—125).—Sufficient material to yield about 1 c.c. of CH_4 is weighed, 0·5 c.c. of anethole added, and introduced into a micro-gas-evolution apparatus in which the air is displaced by N_2. A known vol. of Grignard reagent is introduced and the CH_4 evolved is measured. Excess of NH_2Ph is then added and the amount of CH_4 now produced indicates the amount of reagent unconsumed. Details of apparatus and prodecure are described. J. W. S.

Micro-analytical determination of oxygen in organic substances. H. Hennig (Chem. Fabr., 1936, 9, 239—241).—The material is hydrogenated by combustion in H_2, freed from O_2 by hot Cu, in presence of a Ni catalyst carried on pumice at 400—420°. J. S. A.

Determination of small quantities of an organic substance in the air. T. Brehmer (Suomen Kem., 1936, 9, B, 14).—The author's method (A., 1935, 876) is used to determine the v.p. of $C_{10}H_8$ at 15° to 40·5°; results are in agreement with the literature. Org. halogen compounds are determined by making the compound react with a metal or metallic oxide (of which the corresponding carbonate has low CO_2 pressure), or with a metallic carbonate (of high CO_2 pressure). On applying the necessary corrections, the vals. of the v.p. of *p*-$C_6H_4Br_2$ at 17·8° to 23° given by the two methods are concordant. E. W. W.

Coloured crystalline precipitates.—See this vol., 812.

Determination of citric acid in presence of certain organic substances. A. I. Kogan and S. D. Schtipelman (J. Appl. Chem. Russ., 1936, 9, 568—571).—3—4 ml. of buffer solution (49 g. of H_3PO_4 and 68 g. of KH_2PO_4 per litre) are added to 100 ml. of solution in a flask fitted with a condenser, and 0·05% $KMnO_4$ is added drop by drop to the boiling solution to the appearance of a permanent coloration. MeCHO (from lactic or tartaric acid, glucose, or tannins) is removed from the distillate by adding 5 ml. of 25% H_2SO_4 and 5 ml. of 5% $KMnO_4$, excess of which is eliminated by adding $FeSO_4$, excess of NaOH is added, the vol. is made up to 300 ml., and the solution is filtered. Excess of 0·1*N*-I in KI is added to 100 ml. of filtrate, the solution is shaken for 15 min., made acid with H_2SO_4, and excess of I is titrated. The method depends on the reactions: citric acid$\rightarrow COMe_2$; $6NaOH+6I \rightarrow 3NaI+3NaOI$; $COMe_2+3NaOI \rightarrow CHI_3+NaOAc+2NaOH$. R. T.

β-Naphthoylhydrazine as a reagent for the identification of aldehydes and ketones. H. Chen and P. P. T. Sah (J. Chinese Chem. Soc., 1936, 4, 62—68).—β-$C_{10}H_7{\cdot}CO_2Et$ with N_2H_4,H_2O in boiling EtOH affords β-naphthoylhydrazine (cf. A., 1932, 847) which with the theoretical amount of aldehyde or ketone in 95% EtOH containing a little AcOH gives the hydrazone. β-*Naphthoylhydrazones* (m.p. in parenthesis) of the following are prepared: MeCHO (109—110°); EtCHO (165—166°); $Pr^{\alpha}CHO$ (187—188°); $Pr^{\beta}CHO$ (146—147°); $Bu^{\alpha}CHO$ (158—159°) *n*-hex- (96—97°) and *n*-heptaldehyde (114—115°); PhCHO (213—214°); *m*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ (234—235°); 5-methylsalicylaldehyde (196—197°); furfuraldehyde (199—200°); $COMe_2$ (145—146°); Me hexyl ketone (84—85°); COPhMe (201—202°); *p*-bromo- (219—220°), *p*-methyl- (181—182°), and *p*-methoxy-acetophenone (210—211°); Et (135—136°) and benzyl lævulate (111—112°), and lævulic acid (142—143°). Primary and *sec.* alcohols are identified after oxidation. J. L. D.

***m*-Bromobenzhydrazide as a reagent for the identification of aldehydes and ketones.** Chung-Hsi Kao, T. Tao, Cheng-Heng Kao, and P. P. T. Sah (J. Chinese Chem. Soc., 1936, 4, 69—74; cf. A., 1934, 790).—*m*-Bromobenzhydrazide (A., 1899, i, 136) with aldehydes or ketones in boiling 95% EtOH gives m-*bromobenzoylhydrazones*. Derivatives (m.p. in parenthesis) are prepared from: MeCHO (160—161°); EtCHO (135—136°); $Pr^{\alpha}CHO$ (97—98°); $Bu^{\alpha}CHO$ (88—89°); *n*-hept- (71—72°), *m*-nitrobenz- (217—218°), and *p*-nitrobenz-aldehyde (240—241°); furfuraldehyde (197—198°); 5-methylsalicylaldehyde (222—223°); cinnamaldehyde (210—211°); CH_2Ac_2 (126—127°); COPhMe (162—163°); *p*-methyl- (188—189°) and *p*-methoxy-acetophenone (163—164°); $COPh_2$ (128—129°); lævulic acid (155—156°); benzyl lævulate (102—103°). J. L. D.

Reduction of silver nitrate by cuprous oxide applied to the determination of reducing sugars. V. Harlay (J. Pharm. Chim., 1936, [viii], 23, 589—594).—Glucose with an alkaline Cu salt ppts. Cu_2O which is determined with $AgNO_3$. J. L. D.

Analytical uses of Nessler's reagent. M. Goswami and B. C. Das-Purkayastha (J. Indian Chem. Soc., 1936, 13, 73).—Fructose and sucrose have been determined by the method previously described (this vol., 745). E. E. A.

Azides. V. 3-Nitrobenzazide as a reagent for the identification of amines. K. Meng and P. P. T. Sah (J. Chinese Chem. Soc., 1936, 4, 75—79; cf. A., 1934, 997; 1935, 207).—3-Nitrobenzazide with an amine in dry hot PhMe gives a carbamide. *Carbamides* are prepared (m.p. in parenthesis) from the following: *o*- (227—228°) and *p*-nitro- (270—271°), *p*-chloro- (212—213°), and *p*-bromo-aniline (257°); NHPhEt (104 105°); *o*- (214—215°), *m*- (191—192°), and *p*-$C_6H_4Me{\cdot}NH_2$ (202—203°); *m*-nitro-*p*-toluidine (213—214°); α- (238—239°) and β-$C_{10}H_7{\cdot}NH_2$ (245—246°); NHPhAc (135—136°); *p*-$C_6H_4Br{\cdot}NHAc$ (152°); acet-*o*- (233—234°) and -*p*-toluidide (241—242°); *m*-bromo-*p*-toluidine (192—193°). J. L. D.

Reactions of cystine and materials containing cystine. A. Steigmann (Phot. Ind., 1935, 33, 445—446; Chem. Zentr., 1935, ii, 1486).—A reaction is given, in conjunction with the Feigl and albumin reactions, for the sp. identification of cystine, keratoses, albumins, and albumoses. J. S. A.

Precipitation of cystine.—See this vol., 881.

Separation of amino-acids. V. Recovery of Japanese acid clay [after use for adsorption of] amino-acids. M. Mashino and N. Shikazono (J. Soc. Chem. Ind. Japan, 1936, 39, 136B; cf. this vol., 561).—The NH_2-acid is removed with CaO and the clay washed with the theoretical amount of HCl and then with H_2O. The total N, but not the protein-N, adsorbed decreases with repeated use of the clay. Recovery of the protein by CaO is complete after the first adsorption. R. S. C.

Determination of camphor as 2 : 4-dinitrophenylhydrazone in concentrated and dilute alcoholic solutions of camphor. M. M. Janot and M. Mouton (J. Pharm. Chim., 1936, [viii], 23, 547—549).—The method of Hampshire and Page (B., 1935, 253) is examined and modified, and is compared with that of Bougault and Leroy (B., 1928, 690). E. W. W.

Micro-determination of uric acid. N. L. Edson and H. A. Krebs (Biochem. J., 1936, 30, 732—735).—A method for conversion of uric acid (I) by way of allantoin and allantoic acid into a mixture of $CO(NH_2)_2$ (II) and $CHO{\cdot}CO_2H$ (III) is described. Either end product can then be determined, (III) either colorimetrically or by HSO_3'-titration and (II) by various methods. In determinations of 0·1—2·0 mg. of (I), (II) is determined manometrically using urease, the method being sp. and having a const. error of $8\pm3\%$ which is corr. for. The method is particularly suitable for use in conjunction with tissue slice work but is not suitable for blood analysis or for solutions containing $<$ 0·1 mg. of (I) per 5 ml. of fluid. P. W. C.

The Vitali reaction: new technique permitting micro-determination of substances giving the reaction. C. Morin (J. Pharm. Chim., 1936, [viii], 23, 545—547).—When atropine or hyoscyamine is evaporated with fuming HNO_3 and the residue dissolved in anhyd. $COMe_2$ and treated with 10% MeOH–KOH, an intense and comparatively stable violet coloration results, by means of which small quantities of the alkaloid may be determined colorimetrically. E. W. W.

Determination of the number of replaceable hydrogen atoms in strychnine, vomicine, and phloroglucinol. H. Erlenmeyer, A. Epprecht, and H. Lobeck (Helv. Chim. Acta, 1936, **19**, 543—545).—Strychnine nitrate, vomicine nitrate, and phloroglucinol exchange 1, 3, and 6 H, respectively, for D, when cryst. from 99·6% D_2O. R. S. C.

Determination of total basic amino-acids in gelatin by titration in glacial acetic acid. J. Russell and A. E. Cameron (J. Amer. Chem. Soc., 1936, **58**, 774—775).—Titration of a gelatin (dissolved in a little H_2O and then diluted with AcOH) with 0·0119*N*-$HClO_4$ using a H electrode indicates the presence of $9·6\times10^{-4}$ equiv. of dibasic NH_2-acids per g. Titration curves for lysine and arginine in AcOH are given. H. B.

Biochemistry.

Relations between oxygen consumption, carbon dioxide production, and expired air during respiration in man. J. Joanid and F. Nepveux (Compt. rend. Soc. Biol., 1936, **121**, 1618—1620).—CO_2 production $\propto$ ventilation, but O_2 consumption is const. R. N. C.

Determination of basal metabolism in the adult pigeon during nutritional studies. R. Lecoq and J. M. Joly (Compt. rend. Soc. Biol., 1936, **122**, 193—195).—The R.Q. can be determined by direct measurement of O_2 consumed and CO_2 produced. A coeff. is given to determine the surface area of the body. R. N. C.

Absorption of dust through respiration. II. Absorption of pyrolusite dust. O. Ehrismann (Z. Hyg., 1935, **117**, 662—678).—MnO_2 is adsorbed by rabbits and cats exposed to pyrolusite dust, but there is no essential increase of Mn in the organs, particularly the lungs. R. N. C.

Permeability of the mammalian erythrocyte to deuterium oxide (heavy water). A. K. Parpart (J. Cell. Comp. Physiol., 1935, **7**, 153—162).—The rate of penetration of ox and rat erythrocytes by 99·5% D_2O is about 44% $<$ that by H_2O; the permeability is apparently uninjured by D_2O. R. N. C.

Permeability of erythrocytes to deuterium oxide (heavy water). S. C. Brooks (J. Cell. Comp. Physiol., 1935, **7**, 163—171).—The rate of hæmolysis of sheep erythrocytes by solutions containing D_2O is $<$ that by H_2O alone, given equal concn. gradients. This is due largely to differences in fugacity. R. N. C.

Osmotic properties of the erythrocyte. VII. Temperature coefficients of certain hæmolytic processes. M. H. Jacobs, H. N. Glassman, and A. K. Parpart (J. Cell. Comp. Physiol., 1935, **7**, 197—225).—The temp. coeff. of hæmolysis of human, rat, mouse, rabbit, and guinea-pig erythrocytes in isotonic glycerol solution is low. Hæmolysis is rapid, and is retarded by CO_2, acids, and traces of Cu, the temp. coeff. being increased. Ox, sheep, swine, horse, dog, and cat erythrocytes show slow hæmolysis, high temp. coeff., and often acceleration of hæmolysis by acids and Cu. R. N. C.

Permeability of red blood corpuscles to organic anions. R. Höber (J. Cell. Comp. Physiol., 1936, **7**, 367—391).—Penetration of anions across a collodion membrane is $>$ that expected from the migration velocity, due to surface activity in the case of fatty acids, and the hydrotropic properties in the case of sulphonates and aromatic anions. Anions of OH- and polybasic acids lack these properties and are rather inactive. The permeability of the red cell membrane is similar, but the presence of lipins facilitates the entrance of fatty and aromatic anions, particularly with sheep and ox corpuscles. R. N. C.

Magnetic properties and structure of hæmoglobin, oxyhæmoglobin, and carboxyhæmoglobin.—See this vol., 867.

Hæmocuprin from hæmocyanins. J. Roche and P. Dubouloz (Compt. rend. Soc. Biol., 1936, **122**, 234—236).—Hæmocuprin is a polypeptide containing tyrosine, arginine, and leucine. R. N. C.

Isoelectric point of fibrinogen. E. Kylin and F. Paulsen (Biochem. Z., 1936, **285**, 159—174).—Fibrinogen (I) yields an acid and two basic fractions on subjection to cataphoresis. One basic fraction (min. stability at p_H 7·3 and $<$ 12·4) is colourless, is coagulated by heat at 55°, and is pptd. on 28% saturation with $(NH_4)_2SO_4$, saturation with $MgSO_4$, and half saturation with NaCl. The other (min. stability at p_H 7·3) is white, is coagulated by heat at 37°, and is pptd. on 16% saturation with $(NH_4)_2SO_4$, half saturation with $MgSO_4$, and 33% saturation with NaCl. The isoelectric points are: acid fraction p_H 5·4, basic fractions 12·4 and 8·5, respectively. The theory of ideal ampholytes does not hold for (I). (I) of exudates consists entirely of the second basic fraction. W. McC.

Viscosity of fibrinogen. E. Wöhlisch and A. Kiesgen (Biochem. Z., 1936, **285**, 200—206; cf. this vol., 562).—Fibrinogen (I) (from horse plasma) exhibits anomalous η, the deviation from normal decreasing with rising temp. High concns. of urea reversibly inhibit coagulation of (I) solutions by heat, EtOH, and thrombin (II) and increase η, greatly reducing the abnormality. After extraction with Et_2O the temp. of denaturation of (I) is raised; denaturation with EtOH and heat and coagulation with (II) are more difficult, and η is normal. These results confirm the view that (I) has a fibrous mol. structure. W. McC.

Protein equilibrium of serum during sensitisation and serum shock. Aubry, Thiodet, and Ribère (Compt. rend. Soc. Biol., 1936, **122**, 209—212).—The albumin/globulin ratio increases during sensitisation, falls rapidly at the crisis, and rises again at the end of the reaction. R. N. C.

Precipitation of serum-proteins by ammonium sulphate: arterial hypertension. A. Roche, M. Dorier, and L. Samuel (Compt. rend. Soc. Biol., 1936, **122**, 231—233).—In cases of hypertension, pptn. does not separate albumin (I) and globulin (II), and the (I)/(II) ratio has no significance. The modifications are associated with the nature of the proteins rather than with the (I) and (II) contents of the serum. R. N. C.

Constituents of acid globulins. Protein *C*. M. Doladilhe (Compt. rend., 1936, **202**, 1385—1387).—The serum of human, ox, or sheep blood is aged under sterile conditions for 4—5 days at 0°; the acid globulins therefrom are dissolved in physiological aq. NaCl (1/10 vol. of the serum); CO_2 then ppts. protein *B* and a new *protein C*. The mixed ppt. is redissolved in aq. NaCl and centrifuged at 45° for 15 min., whereby protein *A* is pptd.; *C* separates on cooling. *C* dissolves in H_2O at higher temp. and is repptd. on cooling, unless the solution has been heated above a certain temp. This crit. temp. is usually 55°, but is higher if the ageing of the serum has been prolonged (*e.g.*, 8—15 days) or slightly less if *B* has been heated at too high a temp. (which also decreases the pptn. of *C* by CO_2). *C* is a constituent of group *B* and a probable factor of complement. Ageing and heat diminish the physiological effects of the latter in serum at the same time as affecting the physical properties of the former. R. S. C.

Biochemistry of choline and its derivatives. I. Acetylcholine in blood. E. Kahane. **II. Biological determination of acetylcholine.** J. Lévy and L. Olszycka. **III. Determination of acetylcholine in biological material. IV. Action of blood on esters of quaternary ammonium compounds.** E. Kahane and J. Lévy (Bull. Soc. Chim. biol., 1936, **18**, 479—489, 490—504, 505—528, 529—555).—I. Introductory.

II. The method makes use of the fact that 0·03—$0·2 \times 10^{-6}$ g. of acetylcholine (I) may be detected by the fall in blood pressure produced on intravenous injection into chloralised dogs. The effect of the material to be determined is compared with that produced by (I) chloride. Eserine sulphate (II) may be used to increase the reaction of the animals.

III. The above method is applied to the determination of (I) added to serum and blood. The technique of chemical methods of determining (I) involving hydrolysis and pptn. as phosphotungstate, silicotungstate, Reineckate, and periodate is described. The pharmacological method may also be applied to these ppts.

IV. Propionyl-, formyl-, and acetyl-choline are rapidly hydrolysed by serum; betaine Et ester, acetyl-β-methylcholine, and benzoylcholine are slowly attacked, and bromocholine and the nitric and carbamic esters of choline are not hydrolysed. Injections of (II) only increase the hypotensive action of those esters which are rapidly hydrolysed. A. L.

Acetylcholine-like substance dissimulated in normal blood. E. Kahane and J. Lévy (Compt. rend., 1936, **202**, 1210—1212).—The fluid obtained when blood is treated with boiling H_2O and then EtOH contains an acetylcholine-like substance (0·01—$1·5 \times 10^{-5}$ g. per c.c.) which is not ultrafilterable and may be the precursor of acetylcholine. J. L. D.

Blood-glutathione and pulmonary respiration. L. Binet and S. Barret (Compt. rend. Soc. Biol., 1936, **122**, 16—18).—Perfusion of a dog's lung ventilated with O_2 diminishes the reduced glutathione (I) content of the blood. In N_2 (I) increases, subsequent ventilation with O_2 decreasing it again. R. N. C.

Determination of indole in blood. P. Mazzocco (Rev. soc. argentina biol., 1935, **11**, 31—37).—Oxalated blood (1 c.c.) is extracted successively with 3, 2, 2, and 1 c.c. of Et_2O and the combined extract is diluted to 12 c.c. with EtOH. *p*-$NMe_2 \cdot C_6H_4 \cdot CHO$ (10 drops of 5% EtOH solution) followed by 2 c.c. of conc. HCl are added and the colour is matched against a standard. Blood-urobilinogen interferes since it gives a red colour.

Ch. Abs. (*p*)

Extraction of blood-lipins. E. M. Boyd (J. Biol. Chem., 1936, **114**, 223—234).—The limitations of the Bloor lipin extractions (A., 1915, ii, 805) are investigated. For aliquots $>$ 3 c.c. 20 vols. of EtOH–Et_2O for plasma and 30 vols. for whole blood are required; warming and variation of the EtOH : Et_2O ratio were without influence. Oxalated plasma had higher vals. than defibrinated serum. H. D.

Relationship between total and free cholesterol in human blood-serum. W. M. Sperry (J. Biol. Chem., 1936, **114**, 125—133).—In 126 samples of serum from 91 healthy adults, the min. amount of free in total cholesterol (I) was 24·3% (max. 30·1%; average 26·9%). Most samples taken after sudden death gave vals. within the same range. Similar results were obtained in healthy children and in 80% of diseased children. The % of free (I) in total (I) may be of val. in the study of (I) metabolism and in pathology. J. N. A.

Blood-cholesterol in rabbits painted or injected with benzopyrene. Y. Pourbaix and N. Denisoff (Compt. rend. Soc. Biol., 1936, **122**, 128—130).—There is no appreciable variation. R. N. C.

Normal blood-sugar in domestic animals. A. S. Campori (Rev. Med. vet. Buenos Aires, 1935, **17**, 47—75).—The vals. were: cows 40—70, horses 50—100, asses 40—100, cats 50—120, dogs 50—100, poultry 100—214 mg. per 100 ml. Nutr. Abs. (*m*)

Fasting blood-sugar in rats. E. M. Greisheimer, E. George, and L. Gilman (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1669).—The rate of decrease of blood-sugar in females is $>$ in males, and is greatest in both sexes between 12 and 24 hr. R. N. C.

Rapid methods of blood-sugar determination with potassium ferricyanide. C. H. Hagedorn, F. Halstrom, and N. Jensen (Hospitalstidende, 1935, **78**, 1193—1202).—To 0·1 or 0·05 ml. of blood are added 1 ml. of 0·1*N*-NaOH and 5 ml. of 0·45% aq. $ZnSO_4$, the mixture is heated at 100° for 4 min., and after cooling, filtered through purified cotton wool. Then 2 ml. of alkaline 0·005*N*-$K_3Fe(CN)_6$ are added and the mixture is heated for 5 min. at 100°. When cold, KI is added, then 1 ml. of citric acid and $ZnSO_4$ reagent, and the I liberated titrated with 0·005*N*-$Na_2S_2O_3$. Rapidity is increased by heating in an open flask and using tablet reagents.

Nutr. Abs. (*m*)

Widmark's method of blood-alcohol determination. H. Elbel (Deut. Z. ges. gerichtl. Med., 1935, **25**, 124—129; Chem. Zentr., 1935, ii, 1585).—Methods for increasing the accuracy are described. H. N. R.

Variations of blood-copper in normal children at different ages. E. Lesné, P. Zizine, and S. B. Briskas (Compt. rend. Soc. Biol., 1936, **121**, 1582—1583).—Blood-Cu falls after birth, fluctuates at $<$ 1 mg. per litre in the first 10 days, and then increases to a steady val. of 1·35 mg. per litre in the first or second month. R. N. C.

Determination of total iron in blood. F. B. Shorland and E. M. Wall (Biochem. J., 1936, **30**, 1047—1048).—The blood (0·5 ml.) is digested with H_2SO_4–HNO_3 and the Fe determined by a modification of the 2 : 2′-dipyridyl method. J. N. A.

Action of certain reagents on the "loosely bound" iron in blood. F. B. Shorland and E. M. Wall (Biochem. J., 1936, **30**, 1049—1052).—Thioacetic acid has a definite action on hæmoglobin-Fe (I) and cannot be used for determination of non-hæmoglobin-Fe (II). $Na_4P_2O_7$ does not attack (I) and gives a good recovery of inorg. Fe added to blood. The vals. obtained for (II) by use of $Na_4P_2O_7$ are much lower than those obtained by Starkenstein and Weden's method (A., 1928, 1275). J. N. A.

Iron content and oxygen capacity of blood. M. Johnson and M. E. Hanke (J. Biol. Chem., 1936, **114**, 157—170).—An iodometric method by which the Fe in blood may be determined to 10^{-6} g. per litre of blood is described. To obtain this accuracy, complete oxidation of the blood, removal of SO_4'' and PO_4''', and control of the concn. of acid and salts for the $Na_2S_2O_3$ titration are essential. The conversion factor for $Na_2S_2O_3$ must be determined with standard $FeCl_3$, as it varies with the amount of Fe. The end-point must be determined under standardised conditions as regards amounts of KI and time intervals. The Fe content and O_2 capacity of blood agreed within 1%. J. N. A.

Determination of lead in blood. Anon. (Chem.-Ztg., 1936, **60**, 368).—Various methods are described. F. O. H.

Iodometric determination of chloride in small amounts of blood. G. A. D. Haslewood and E. J. King (Biochem. J., 1936, **30**, 902—905).—The method uses the fact that on adding $AgIO_3$ in aq. NH_3 solution to solutions containing Cl′, an amount of IO_3' equiv. to the Cl′ passes into solution, which on determination iodometrically liberates 6I for each Cl′ originally present. The method is used for determinations of pure NaCl and of Cl′ in $Zn(OH)_2$ filtrates of 0·2 ml. of blood or plasma, the results in the latter case agreeing within 1% amongst themselves and with gravimetric analyses. P. W. C.

Effect of diet on blood-phosphorus partition of rats with or without insulin. N. van Cleve and A. F. Morgan (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1636—1641).—Insulin evokes a decrease of inorg. P only in animals on a high-fat diet. Other determined P fractions vary only slightly; total P is unchanged and org. P tends to increase. R. N. C.

Distribution of phosphorus compounds in human and animal blood. H. Nissen (Z. Kinderheilk., 1935, **57**, 289—320; Chem. Zentr., 1935, ii, 1571).—Analytical vals. are given for the different P fractions in the blood of man and a no. of animals. R. N. C.

Acid–base condition of blood. V. Influence of protein concentration on the colorimetric p_H determination of blood-serum. H. W. Robinson, J. W. Price, and G. E. Cullen (J. Biol. Chem., 1936, **114**, 321—340).—The influence of the protein concn. on the correction to be applied to the determined val. of serum-p_H by Cullen's method (A., 1922, ii, 672) is studied by comparing the p_H vals. of sera conc. by ultrafiltration and diluted with the ultrafiltrate. The correction $\propto$ log protein concn. H. D.

Determination of the p_H of blood with the glass electrode. G. Haugaard and E. Lundsteen (Biochem. Z., 1936, **285**, 270—281).—Methods of determining the p_H of venous and capillary blood are described. Determinations must be made $\ngtr$ 5 min. after drawing the blood. Part of the titration curve of venous blood has been plotted. W. McC.

Anion and cation contents of normal and anæmic blood. M. Maizels (Biochem. J., 1936, **30**, 821—830).—The concn. of anions and cations ($K^{\cdot}$, $Na^{\cdot}$, HCO_3', and Cl′) in erythrocytes is $<$ that in plasma, the resulting deficiency in cellular osmotic pressure indicating binding of approx. 8% of the cell-H_2O. The excess of base over $Cl'+HCO_3'+Hb'$ in the cells indicates the presence of another anion which is increased in anæmia but not in acholuric jaundice. Concn. of cell-cation is relatively const. despite wide variations in cell-Hb and in blood regeneration and destruction. Cellular changes in acholuric jaundice are discussed. F. O. H.

Ionisation and buffers of the internal medium of the parasitised sacculenised crab (*Carcinus mænas*). A. Drilhon and E. A. Pora (Compt. rend., 1936, **202**, 1309—1311).—The parasite causes a disappearance of the buffering substances of the serum, whereas the presence of the large amount of CO_2 in the hæmolymph maintains a high alkaline reserve and lowers the p_H. H. G. R.

Composition of arterial blood after ingestion of saline solution. P. Cambier and G. Bardos (Compt. rend. Soc. Biol., 1936, **122**, 130—132).—Ingestion of Priestley's solution causes dilution of the blood with only feeble diuresis compared with that from ingestion of H_2O. R. N. C.

Water content of the blood of the normal human adult. Correlation between the water content of blood from the ear lobe and that from the median vein. T. Ryô (Keijo J. Med., 1935, **6**, 9—22).—Average vals. were 79·25% for the ear and 79·74% for the median vein. Ch. Abs. (*p*)

Water content of the blood of chicken during the course of development. K. Kuroda (Keijo J. Med., 1935, **6**, 23—29).—Max. vals. were observed at hatching; a min. at 2 weeks was followed by a second max. and a subsequent decline to a const. level. Ch. Abs. (*p*)

Lipin films in relation to the structure of the plasma membrane. J. F. Danielli (J. Cell. Comp. Physiol., 1936, 7, 393—407).—Continuous lipin and mosaic films are all metastable, the lipin films being the more stable. The prep. of shell-lipin films is described. R. N. C.

Spontaneous reversibility of the gelation of serum. I. Kopaczewska, W. Kopaczewski, and S. Marczewski (Compt. rend., 1936, 202, 1212—1214).—Normal human serum in H_2O gels in presence of 0·1—0·3*N*-NaOH. The optimum rate of gelation for any concn. of serum occurs with only one [NaOH]. The gel liquefies, the rate being greatest when [NaOH] is high and the serum is very dil. J. L. D.

Gelation of human serum by bases. S. Marczewski (Compt. rend., 1936, 202, 510—511; cf. A., 1935, 374).—The period of gelation by NaOH and various org. bases decreases with rising temp. Certain bases (toluidine, PhOH) have no direct action, but accelerate gelation by other bases. Still other bases, even at high concns., are ineffective. Factors other than [OH′] are concerned in gelation. A. G. P.

Relations between electric charge and hydration of flocculation of blood-serum. R. Jonnard (Compt. rend. Soc. Biol., 1936, 122, 48—50).—The curve of the EtOH/acid ratio for flocculation to begin and the acid concn. is almost a rectangular hyperbola. The ratio at any given acid concn. is const. and independent of the serum concn. R. N. C.

Nature of agglutinogens. G. Bruynoghe (Compt. rend. Soc. Biol., 1936, 122, 94—95).—The *A* and *B* isoagglutinogens are proteins, whilst the *M* and *N* supplementary agglutinogens are lipins. R. N. C.

Mode of formation of aggregates in bacterial agglutination. W. W. C. Topley, J. Wilson, and J. T. Duncan (Brit. J. Exp. Path., 1935, 16, 116—120).—Experimental data throw doubt on the view that flocculation occurs in two stages, one sp. and one non-sp., but accord well with Marrack's lattice theory. Ch. Abs. (*p*)

Relation between the complement and opsonin of normal serum. J. Gordon and F. C. Thompson (Brit. J. Exp. Path., 1935, 16, 101—108).—Treatment of serum with NH_3, Congo-red, acid, alkali, or with hypertonic solutions of certain Na or K salts, or long storage at room temp. may inactivate the complement without affecting the concn. of opsonin. The latter is non-sp. and thermolabile, and resembles the complement in many respects, but is probably an independent system. Modified complement may possibly function as an opsonin. Ch. Abs. (*p*)

Specificity of hybrid proteins. A. G. Zoet (Proc. Soc. Exp. Biol. Med., 1935, 32, 1469—1470).—Hybridised protein from horse and swine serum is serologically different from the serum-proteins of both species. R. N. C.

Reactivation of ammonia-inactivated complement by leucocytes. E. Maltaner (Proc. Soc. Exp. Biol. Med., 1935, 32, 1555—1558). R. N. C.

Nature of tuberculous antibodies: some properties peculiar to the guinea-pig. K. Meyer (Compt. rend. Soc. Biol., 1936, 122, 26—28).—The production of lipin (I) and protein antibodies (II) in normal guinea-pigs by the Besredka antigen (III) or extracts of tubercle bacilli is similar to that in rabbits, but in tuberculous animals (I) are often absent, whilst (II) react only feebly with the protein antigens, although strongly with (III). R. N. C.

Mechanism of immunity to filterable viruses. I. Does the virus combine with the protective substance in immune serum in the absence of tissue? II. Fate of the virus in a system consisting of susceptible tissue, immune serum, and virus and the rôle of tissue in the mechanism of immunity. A. B. Sabin (Brit. J. Exp. Path., 1935, 16, 70—84, 84—100).—I. There is no apparent union between the virus and the protective substance *in vitro*.

II. Immunity to virus intimately concerns the cell. Both protective substance and virus are fixed by the tissue. If fixation of the virus precedes that of protective substance infection is not prevented. Fixation in the reverse order or simultaneously prevents infection. Ch. Abs. (*p*)

Diffusion potentials in scallop muscles. H. B. Steinbach (J. Cell. Comp. Physiol., 1935, 7, 271—289).—The concn. *E* is the same at the injured and uninjured surfaces, the more dil. solution being positive for KCl but negative for NaCl, $MgCl_2$, or $CaCl_2$. $Ca^{··}$ increases the [KCl] *E* at the injured, but not the uninjured surface. *E* may be termed a diffusion concn. if the tissue is considered as a solution of a colloidal electrolyte. R. N. C.

Nature and permeability of the grasshopper egg membrane. I. E.m.f. across membranes during early diapause. T. L. Jahn (J. Cell. Comp. Physiol., 1935, 7, 23—46).—The apparent relative ionic mobilities of univalent cations across membranes increase in the same order as Λ_t in solution, but the differences are less. Those of bivalent cations fall very rapidly as concn. increases. The concn. effect is reversed by conc. solutions of bivalent ions ($-\log c = 1·3$ approx.), and by HCl solutions at $p_H < 2·1$; the membrane can recover from reversal by $Ca^{··}$, but only incompletely from reversal by HCl. The anion does not influence the concn. effect. *E* across the membrane in *M*- and 0·1*M*-KCl is not affected by p_H between 4 and 6, but below p_H 4 it falls rapidly, reaching zero at p_H 2·2 and then becoming negative; equilibrium is established only slowly below p_H 3. The exochorion and one of the cuticle layers of the egg are semipermeable, the former probably being responsible for *E* changes. *E* shows a definite correlation with the expected changes in potential for a protein surface. R. N. C.

Electrical conductivity of yolk, albumin, and allantoic and amniotic fluids of developing birds' eggs. A. L. Romanoff and H. J. Grover (J. Cell. Comp. Physiol., 1936, 7, 425—431). R. N. C.

Behaviour of the electrical conductivity of the yolk of the hen's egg with change of temperature. A. Orrù (Atti R. Accad. Lincei, 1935, [vi], 22, 458—463).—Egg-yolk does not exhibit the hysteresis of κ at rising and falling temp. observed with gelatin (A., 1930, 993). At 16—18° to 60° a straight-line graph of κ against temp. is obtained on heating the uncoagulated or coagulated yolk. At higher temp., changes of κ indicate a max. (72—76°) due to the coagulation of lecitho-vitellin, a second due to that of livetin, whilst a third is ascribed to a third protein, as suggested by Jukes and Kay (A., 1932, 957). E. W. W.

Relation between acids and bases in the human brain cortex. A. Petrunkina and M. Petrunkin (J. Physiol. Path. gén., 1935, **33**, 1102—1113).—Grey matter of human brain cortex contains a large excess of base combined with the CO_2 and colloids. The isoelectric point of the colloids is at p_H 4·35. Nutr. Abs. (*m*)

Calcium and phosphorus content of the body of the brook trout in relation to age, growth, and food. C. M. McCay, A. V. Tunison, M. Crowell, and H. Paul (J. Biol. Chem., 1936, **114**, 259—263).—The increases of body-Ca are chiefly due to absorption from H_2O. In the eggs and fry [P] is > [Ca]; as soon as the fry start to feed the [Ca] increases rapidly. H. D.

Primary calculi of the smaller intestine. G. Blix (Acta chirurg. Scand., 1935, **76**, 25—34; Chem. Zentr., 1935, ii, 1391).—The calculi contain 58% of CaC_2O_4, 11% of choleic acid, and 1·4% of ZnS. The ZnS is formed from sol. Zn compounds by bacterial action. A. G. P.

Histo-chemical detection of lead in bones. E. Sieber (Arch. exp. Path. Pharm., 1936, **181**, 273—280).—Fixation by 70% EtOH or aq. CH_2O and decalcification by 30% HCO_2H (both saturated with H_2S) indicates the distribution of Pb in bone-tissue of Pb-poisoned guinea-pigs. Variations of Pb distribution with age of Pb-poisoned animals are described. F. O. H.

Chemical composition of the minerals of bone. J. Marek, O. Wellmann, and L. Urbányi (Mezög. kutat., 1935, **8**, 217—225).—H_2O, glycerol (I), aq. KOH, KOH in (I), and aq. K_2CO_3 hydrolyse the Ca–P compound of bones in the same way as they hydrolyse $Ca_3(PO_4)_2$. Hence bone-phosphate must be composed chiefly of $Ca_3(PO_4)_2$ and $CaCO_3$ with small amounts of $Mg_3(PO_4)_2$ and Ca alkali phosphates. Nutr. Abs. (*m*)

Chemical determination of the age of fossilised bones. J. Gangl (Oesterr. Chem.-Ztg., 1936, **39**, 79—82).—Examination by ultra-violet light does not differentiate between fresh and 2000-year-old bones. The nature of the fats (as with "bog-butter") indicates, however, that with increasing age (2500—5500 years) the m.p., sap. val., and, more especially, the acid val. increase, whilst the I val. and glycerol content decrease. These changes are due to initial enzymic action and, to a greater extent, subsequent oxidation. F. O. H.

X-Ray examination of tooth structure. J. Thewlis (Nature, 1936, **137**, 828).—Enamel which is smooth and free from pigmentation contains much preferentially oriented apatite. A tooth is entirely enclosed by a thin layer of hypercalcified tissue which may act as a protecting layer against caries. The arrangement of crystallites at the surface of the enamel generally differs from that of the interior. L. S. T.

Teeth. III. Variations in chemical composition in relation to dental structure. J. H. Bowes and M. M. Murray (Biochem. J., 1936, **30**, 977—984).—With increased hyperplasia the apatite content of the enamel decreased from 92 to 86% with a corresponding increase in some other P compound; in the dentine the val. decreased from 53 to 49%, but the variations were less regular. H. G. R.

Copper content of the embryonic calf liver. Z. Gruzewska and G. Roussel (Compt. rend. Soc. Biol., 1936, **122**, 13—14).—Cu is equally distributed between the sol. and insol. ash, but is apparently contained in a complex which is decomposed only by inorg. acids. The liver-Cu curve is analogous to the Fe curve throughout embryonic development. The Fe/Cu ratio increases with the age of the embryo. R. N. C.

Fatty acids of chrysalis oil. W. Bergmann (J. Biol. Chem., 1936, **114**, 27—38).—Commercial chrysalis oil of *Bombyx mori* slowly deposits glyceryl $\alpha\gamma$-dipalmitate, which is, however, not formed from the oil from living chrysalides. The acids from both oils contain palmitic 20, stearic 4, palmitoleic 2, oleic 35, linoleic 12, and linolenic acid 28%, with < 1% of other saturated and 1—2% of unsaturated acids with > 18 C. The oils contain < 1% of $COMe_2$-insol. matter. Chrysalis oil from *Malacosoma americana* has a similar composition but contains 7·1% of $COMe_2$-insol. phosphatide. R. S. C.

Lipins of retina, brain, and blood. P. J. Leinfelder and P. W. Salit (Amer. J. Ophthalm., 1934, **17**, 619—624).—Methods of sampling and analysis are described. The lipin content of the retina is < of brain but > that of blood. Retinal tissue contains more H_2O and lecithin (%) but less protein and cholesterol than the other two tissues. Glycolipins have equal concn. in retina and brain. The I vals. of extracts of brain and of retina are similar, suggesting a similar rate of metabolism. Ch. Abs. (*p*)

Application of Fujita's method of blood-sugar determination to tissue-sugar. R. Wetzel (Arch. exp. Path. Pharm., 1936, **181**, 259—264).—The method (A., 1932, 75) is modified so as to be applicable to 0·05—1·50 mg. of glucose. Deproteinisation of tissue hydrolysates by phosphotungstic acid is permissible when excess of reagent is pptd. (as K_2WO_4) by KCl. F. O. H.

Production of glycogen in the liver from sugars. Y. Otomo (Tôhoku J. Exp. Med., 1935, **27**, 420—433).—In rabbits all sugars caused an increase in liver-glycogen as follows: glucose> fructose>galactose>sucrose>maltose>lactose. Intravenous injection gave in most cases higher vals. than did oral administration. Nutr. Abs. (*m*)

Osmotic pressure of glycogen solutions. H. B. Oakley and F. G. Young (Biochem. J., 1936, **30**, 868—876; cf. A., 1935, 297).—Solutions of glycogen from rabbit liver and muscle and methylated rabbit-liver glycogen in 0·1*N*-$CaCl_2$ gave osmotic pressures

indicating a mean particle wt. of the order of 2×10^6. A solution of methylglycogen in C_6H_6 contained particles of the same order of magnitude ($3{\cdot}4\times10^6$). The significance of these results is discussed.
J. N. A.

Determination of muscle-glycogen. H. Bierry, B. Gouzon, and C. Magnan (Compt. rend. Soc. Biol., 1936, **122**, 4—6).—The tissue is dissolved in 30% KOH by autoclaving at 110°, and glycogen (I) is pptd. with hot EtOH and removed by centrifuge. (I) is then hydrolysed with HCl at 120°, the solution is neutralised and deproteinised with $Hg(NO_3)_2$, excess of Hg being removed with Cu, and glucose determined by the micro-Bertrand method.
R. N. C.

Carbohydrate groups of submaxillary mucin. G. Blix (Z. physiol. Chem., 1936, **240**, 43—54).—The mucin (I) yields only traces of H_2SO_4 on hydrolysis, indicating absence of mucoitinsulphuric acid as prosthetic group. Digestion of EtOH-dried (I) with boiling H_2O, extraction of the H_2O-sol. fraction with MeOH, and fractionation of the extract with Et_2O and light petroleum affords two carbohydrates. One [cryst. and forming 20—25% of (I)] contains hexosamine (1 mol.), an acidic (not hexuronic) group, and two Ac groups and gives a positive Ehrlich reaction; the other [forming 5% of (I)] is neutral, contains hexosamine (1 mol.) and hexose (2 mols.; probably mannose), and is probably of the same type as that from ovo- and serum-mucin. F. O. H.

Carbohydrate groups of some glucoproteins. O. Karlberg (Z. physiol. Chem., 1936, **240**, 55—58).—Mucins from umbilical cord, cornea, and vitreous humour yield only traces of H_2SO_4 on hydrolysis (indicating a low content of mucoitinsulphuric acid) and contain hexose and glucosamine approx. 1 : 1 (mol.). F. O. H.

Amino-acids in human skin. H. C. Eckstein (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1573—1574).—Analytical vals. are given. R. N. C.

Basic amino-acids of human skin. R. J. Block (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1574—1575).—The analytical results agree closely with those of Eckstein (see preceding abstract). R. N. C.

Amino-acid content of cod muscle-protein. E. Abderhalden, E. Baertich, and W. Ziesecke (Z. physiol. Chem., 1936, **240**, 152—162).—All known NH_2-acids (including alanine 5·7, valine 3·7, leucine 7·5, glutamic acid 7·5, arginine 6·8, lysine 8·0, histidine 4·8%) are obtained on hydrolysis of the protein. Glycine (I) [but not other NH_2-acids or polypeptides containing (I)] gives a bluish-violet colour with pyrocatechol. W. McC.

Separation of amino-acids. III—V.—See this vol., 872, 873.

Choline in the animal organism. J. Gautrelet (Bull. Soc. Chim. biol., 1936, **18**, 449—478).—A review of published work. A. L.

Composition of muscle of normal adult pigeons at rest. R. Lecoq and R. Duffau (Compt. rend. Soc. Biol., 1936, **122**, 180—182).—H_3PO_4, total acid-sol. P, and adenylphosphoric acid show const. vals. for all the birds tested. Lactic acid and total reducing substances vary over a small range, whilst the readily hydrolysed phosphoric esters, particularly creatinephosphoric acid, vary considerably.
R. N. C.

Bence-Jones proteinuria. L. Meyler (Arch. Int. Med., 1936, **57**, 708—713).—Bence-Jones protein is present in normal bone-marrow probably in the lymphocytes and other leucocytes. H. G. R.

Crystalloids of the mammary gland. J. Grynfeltt (Compt. rend., 1936, **202**, 1300—1302).—These are present in the gland when colostrum is secreted and appear to be due to pptn. of protein.
H. G. R.

Determination of particle weight and shape from diffusion and viscosity data. A. Polson (Nature, 1936, **137**, 740).—Mol. wt. and shape of proteins have been determined from the diffusion const. and η by the formulæ given. For ovalbumin, lactoglobulin, serum-albumin, amandin, thyroglobulin, and octopus hæmocyanin the particle wts. are approx. 0·71 of those obtained from sedimentation data.
L. S. T.

Carotenoids of human serum and liver. I. H. Willstaedt and T. Lindqvist (Z. physiol. Chem., 1936, **240**, 10—18).—Chromatographic separation of serum-carotenoids indicated, in addition to that of β-carotene, the occasional presence of lycopene, zeaxanthin, and xanthophyll; these and, in one case, violaxanthin also occurred in the liver. Two unknown pigments with absorption max. at respectively 498, 468, 422, and 478, 559 in light petroleum, and 512 (?), 498, 470, and 493, 472 mμ in CS_2 occurred in serum and liver; their probable nature is discussed. F. O. H.

Colouring matter of the shell of the cassowary's egg. D. Dinelli (Atti R. Accad. Lincei, 1936, [vi], **22**, 464—467).—The residue after treating the powdered shells with 5% HCl is extracted by MeOH, and the solution treated with MeOH–HCl. The green pigment obtained on evaporation is taken up in Et_2O and extracted with 0·5% aq. HCl. The neutralised product yields a mixture, decomp. 90—100°, which gives an absorption band at 650 mμ, but does not fluoresce after treatment with NH_3 and $Zn(OAc)_2$ (cf. A., 1931, 1066). The residue after the original MeOH extraction is also green; treated with 10% NaOH and acidified, it evolves H_2S and yields a green chromoprotein (N 14·3%). E. W. W.

Cytochrome-*c*. II. Preparation and properties. H. Theorell (Biochem. Z., 1936, **285**, 207—218; cf. A., 1935, 1277).—Simplified methods of purification involving pptn. with $(NH_4)_2SO_4$ and adsorption on $BaSO_4$ and Cellophane followed by elution with HCl and pptn. with $COMe_2$ are described. Purest cytochrome-*c* (I), mol. wt. 16,500, contains C 49·18, H 7·73, O 27·5, N 14·4, S 1·18, Fe 0·34%, and has isoelectric point p_H 9·82 (borate buffer) and 9·86 (glycine–NaOH). At p_H 7·0—9·3 the ionic mobility is independent of $[H^{\cdot}]$. Dried (I) does not deteriorate on keeping and is not destroyed by *N*-HCl and *N*-NaOH. Reduced (I) exhibits absorption max. at 550, 540, 520, 470, and 415 mμ and bands at 345 (weak), 316 (strong), and 275 mμ, whilst oxidised (I) exhibits bands at 520—550, 407, 364, and 276 mμ. In H_2O at $p_H < 2{\cdot}5$ oxidised (I) exhibits one band only at 515—545 mμ and at $p_H > 13$ it exhibits bands at 570—580, 525—545 mμ, the changes which produce these spectroscopically different forms of (I) being reversible. The change to the acid form is accompanied by a red–brown colour change. W. McC.

Constituents of the adrenal gland. III, IV.—See this vol., 704, 854.

Ostacin-ovo-ester from lobsters.—See this vol., 872.

Substance *P*, the atropine-resistant, intestine-stimulating, and vaso-dilating substance from intestine and brain. U. S. von Euler (Arch. exp. Path. Pharm., 1936, **181**, 181—197).—The active principle (cf. Gaddum and Schild, A., 1935, 780), extracted from tissues by $EtOH–H_2SO_4$ and purified by half-saturation with $(NH_4)_2SO_4$ and fractional pptn. from EtOH solution with $COMe_2$ until active in dilutions of $1 : 3 \times 10^6$ on the isolated rabbit's intestine, is unstable to 0·1*N*-NaOH at 100° and tryptic hydrolysis, but relatively stable to acids. Electrodialysis etc. indicate an albumose nature. Its physiological activity and reactions to base-precipitants are discussed. F. O. H.

"Methæmoglobin-production" test for assaying antianæmic potencies of liver extracts. W. Deutsch and J. F. Wilkinson (Brit. J. Exp. Path., 1935, **16**, 33—39).—No correlation exists between results of clinical tests of hæmopoietic potency and ability to form methæmoglobin as determined spectroscopically or by the respirometer. The antianæmic principle of liver is not identical with, and occurs independently of, the methæmoglobin-producing factor. Ch. Abs. (*p*)

Action of ultra-violet light on villikinin. G. von Ludány (Biochem. Z., 1936, **285**, 192—194; cf. this vol., 518).—Secretin (I) and villikinin (II) are not identical, since (I) but not (II) is destroyed by ultra-violet light. W. McC.

Physiology of milk and butter-fat secretion. I. Milk pressure in the udder. II. Development and evolution of milk secretion. J. Hammond (Vet. Rec., 1936, **16**, 519—527, 528—535).—II. During the development of milk secretion the composition of the milk changes. Globulin (I) and albumin (II) appear first, but decrease as the rate of secretion increases; at the same time H_2O, lactose (III), casein (IV), and ash increase. (III) increases faster than (IV). The milks of different species generally show the same proportional composition as that of cow's milk in course of development at similar (I) and (II) levels. A parallel can be drawn between changes in the development of constitution of milk in the individual and the changes that have occurred during the course of evolution in different species. R. N. C.

Electrical resistance of milk and its constituents. B. Luyet (Compt. rend. Soc. Biol., 1936, **122**, 64—65).—*R* is a property of the whey, cream or casein increasing it without altering it essentially. R. N. C.

Ultracentrifugal and electrophoretic studies on the milk-proteins. I. Preliminary results with fractions from skim-milk. II. Lactoglobulin of Palmer. K. O. Pedersen (Biochem. J., 1936, **30**, 948—960, 961—970).—I. A method for calculating sedimentation equilibrium concn. from *n* data by the method of Lamm (A., 1929, 129, 1234) is described. In milk-plasma, the caseinogen (I) is present as a coarse polydisperse system, and the degree of dispersity in solution in PO_4''' buffer depends on the concn. of (I). Milk-serum contains the low-mol. wt. protein of Kekwick, Palmer's lactoglobulin (II) (A., 1924, 434), and lactoglobulin.

II. (II) is homogeneous, mol. wt. about 39,000 and isoelectric point in OAc′ buffer p_H 5·19. The mol. wt. is const. between p_H 1 and 9, but the sedimentation const. indicated a change in the mol. frictional const. at p_H 5 and 7·5. H. G. R.

Variations in lactose content of milk. W. R. Brown, W. E. Petersen, and R. A. Gortner (J. Dairy Sci., 1936, **19**, 81—92).—Hourly samples show considerable variations in blood-sugar and in lactose contents of milk. Correlation between sugar vals. of blood and milk is highest when milk samples taken 1 hr. after blood samples are considered. A. G. P.

Thiol compounds of milk. C. J. Jackson (J. Dairy Res., 1936, **7**, 29—30).—No sol. ·SH compounds occur in cow's milk. The positive nitroprusside test is attributed to cystine in the protein complex. A. G. P.

Iron and copper content of milk throughout the season, as related to anæmia development in rats. W. E. Krauss and R. G. Washburn (J. Biol. Chem., 1936, **114**, 247—252).—Nutritional anæmia was produced in rats fed exclusively on milk obtained from cows fed on a variety of diets, indicating that the variation of the cow's diet was insufficient to cause profound modifications in the Fe and Cu contents of its milk. H. D.

Alleged occurrence of acetylcholine and adrenaline in cat's saliva. J. Secker (J. Pharm. Exp. Ther., 1936, **56**, 464—465).—Polemical against Larson (A., 1935, 1146). H. D.

Hormone content of saliva. A. I. Weisman and C. C. Yerbury (Endocrinol., 1936, **20**, 103—104).—Anterior pituitary-like and œstrogenic hormones are not present in saliva. R. N. C.

Diastatic activity of rat saliva. E. W. Cohn and M. H. Brookes (J. Biol. Chem., 1936, **114**, 139—145).—Rat saliva contains an enzyme capable of hydrolysing starch to reducing sugars. The amount of these produced was determined in terms of Cu_2O by a photo-electric method. J. N. A.

Determination of bile salts in human bile. R. Goiffon, F. Nepveux, and Chaleil (J. Pharm. Chim., 1936, [viii], **23**, 499—513).—After removal of protein with the Folin–Wu reagent, decolorisation with $FeCl_3$, and subsequent purification, the determination is carried out nephelometrically in $(NH_4)_2SO_4$ suspension. H. G. R.

Differential quantitative analysis of bile acids in bile and in duodenal drainage. H. Doubilet

(J. Biol. Chem., 1936, **114**, 289—308).—The bile acids conjugated with taurine and glycine are determined by the Schmidt–Dart method (A., 1921, ii, 284), the cholic acid by the Gregory–Pascoe reaction (A., 1929, 1114) modified by addition of EtOH to the coloured solutions before comparison, and the total bile acids by pptn. with $FeCl_3$ and determination of the pptd. Fe. From these vals. the concns. of deoxycholic and total free bile acids may be calc. H. D.

Gastric secretion of infants with special reference to pepsin and rennin. B. Andersen (Diss., Copenhagen, 1935, 94 pp.).—Methods of distinguishing between rennin (I) and pepsin (II) and possible sources of error are discussed. (I) is not present in the gastric juice of infants and coagulation of milk is due to (I) alone. Nutr. Abs. (*m*)

Gastric secretion. V. Achlorhydria following partial gastrectomy for ulcer: histamine and the transplanted gastric pouch. E. Klein (Arch. Surg., 1935, **30**, 162—170; cf. this vol., 99).—Phases of gastric secretion are discussed. Partial gastrectomy eliminates the secondary phase due to chemical stimulation of the antrum. In some cases there is true anacidity which does not disappear with histamine, as well as a pseudoanacidity. Ch. Abs. (*p*)

Demonstration of adrenaline in the amniotic liquid and extract of the amniotic membrane in different periods of pregnancy. O. Macchiarulo (Arch. Gynäkol., 1935, **159**, 355—359; Chem. Zentr., 1935, ii, 1570).—Adrenaline cannot be detected in human amniotic extract or fluid or Wharton's gelatin. Traces occur after the 9th month of pregnancy. The hyperglycæmic action of amniotic fluid and extract is due to other active principles. R. N. C.

Micro-test for acetone in urine. J. F. Barrett (Biochem. J., 1936, **30**, 888—889).—About 0·2 ml. of urine (or 2 ml. of blood-filtrate after pptn. with tungstic acid) mixed with 3 ml. of sulphosalicylic acid (5% in 1% aq. Na_2SO_4) is boiled and the vapour passed into dil. Nessler's reagent. $COMe_2$ in concns. $\nless$ 0·01 mg. per ml. produces a creamy ppt. Volatile reducing substances (*e.g.*, CH_2O) interfere, and when such are present 1 drop of 1% aq. NaOCl is added to the reagent, the test being then less sensitive. W. McC.

Experimental variations of sulphur elimination in dogs. J. Gosset and S. Delauney (Compt. rend. Soc. Biol., 1936, **121**, 1616—1617).—The post-operative increase in urinary S excretion is due to muscular trauma; anæsthesia and hyperthermia are without influence. R. N. C.

Canine cystinuria. II. Analysis of cystine calculi and sulphur distribution in the urine. D. F. Green, M. L. Morris, G. F. Cahill, and E. Brand (J. Biol. Chem., **114**, 91—94).—The calculi contained 0·14—0·26% of allantoin and approx. 0·5% of unidentified N. Only 30% of the neutral S present in the urine was cystine-S. H. G. R.

Sulphur metabolism. I. Precipitation of cystine from solutions by mercuric and cuprous chlorides and its recovery, as preliminary to its quantitative determination in urine. G. Medes and K. E. Padis (Biochem. J., 1936, **30**, 941—947).—Recovery of cystine (I) from $HgCl_2$ and Cu_2Cl_2 pptn. by decomp. with H_2S yields 69 and 95%, respectively. If the Cu is pptd with KSCN and C_5H_5N the val. is raised to 100%, but the filtrate is not suitable for determination of (I) with Folin's reagent. Using 8 ml. of solution, 0·24 mg. of (I) may be determined by this method. H. G. R.

Composition of urine in the seal. H. W. Smith (J. Cell. Comp. Physiol., 1936, 7, 465—473).—Urea is the principal N compound, but NH_3, creatinine (I), and creatine (II) are present, (II) being apparently of exogenous origin, since the quantity after a meal of herring is > after a meal of clams. There is no evidence that the seal swallows much sea-H_2O. Simultaneous inulin and (I) clearances are essentially identical, showing the absence of renal (I) secretion. R. N. C.

Determination of creatine in urine. W. D. Langley, M. Rosenbaum, and M. G. Rosenbaum (J. Lab. Clin. Med., 1935, **20**, 972—974).—To the urine (1—2 c.c.) is added 1 c.c. of H_2SO_4 (dropwise with mixing) and the mixture left 2—5 hr. at room temp. A standard solution of creatinine (1 mg. per c.c.) is treated similarly. Subsequently, 20 c.c. of saturated picric acid and sufficient 10% aq. NaOH to neutralise the acid with 1·5 c.c. excess are added. The solutions are compared colorimetrically after dilution to 100 c.c. The method is not applicable to diabetic urines. Ch. Abs. (*p*)

Histidine in human urine. (A) F. Földes. (B) R. Kapeller-Adler (Biochem. Z., 1936, **285**, 294—296, 296; cf. this vol., 362).—(A) Polemical.

(B) A reply. Földes' method is based on the detection of a substance other than histidine itself and hence is untrustworthy. W. McC.

Metabolism of guanyltaurine. Occurrence of glycocyamine in urine. D. Ackermann (Z. physiol. Chem., 1936, **239**, 231—235).—When guanyltaurine (I) is fed to dogs about 8% is recovered unchanged in the urine but no asterubin is produced. The glycocyamine (II) in the urine occurs preformed and is not derived from (I). Allantoin (III) is adsorbed by Lloyd's reagent, but gives no red colour with NaOBr in Sakaguchi's test. Hence (III) can be distinguished from (II). W. McC.

Determination of morphine in urine of opium and morphine addicts: practical applications of the reaction. S. To (Japan. J. Med. Sci., IV, 1935, 8, 93—115).—The min. intake of morphine (I) which gives a positive Fröhde test was 0·01 g. in normal cases and 0·017 g. in addicts. Use of (I) or smoking of opium is readily detected by testing the urine. Ch. Abs. (*p*)

Presence of anti-pernicious anæmia principle in normal human urine. G. E. Wakerlin (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1607—1610). R. N. C.

Occurrence of a new breakdown product of blood pigments (pentdyopent) in the urine. F. Wimplinger (Deut. med. Woch., 1935, **61**, 1072—1074).—Pentdyopent appears regularly in the urine in conditions that lead to elimination of bile pigments. It can appear independently from bilirubin and urobilin. Its absence is diagnostically important, as it indicates absence of liver disease. R. N. C.

Origin of natural crystalline urobilin (stercobilin). C. J. Watson (J. Biol. Chem., 1936, **114**, 47—57).—A cryst. urobilin, not identical with stercobilin, has been obtained from mesobilirubinogen *in vitro*, and the existence of a second urobilinogen in excreta is indicated. H. G. R.

Uropterin, a yellow pigment from human urine. W. Koschara (Z. physiol. Chem., 1936, **240**, 127—151; cf. A., 1935, 774; Schöpf *et al.*, A., 1933, 1311).—The "purine fraction" of normal human urine contains uropterin (I) (concn. 1 : 10^6), which is probably identical with the xanthopterin of the wings of the brimstone butterfly (*Gonepteryx rhamni*). (I) is isolated by adsorption on fuller's earth and elution with aq. C_5H_5N with const. observation of the fluorescence in ultra-violet light. H_2S reduces (I), the leuco-compound produced being re-oxidised by atm. O_2. Xanthopterins occur also in the rabbit, horse, and ox and in hay. W. McC.

Human foot perspiration; nature and inter-reactions with footwear. A. Colin-Russ (J. Hyg., 1935, **35**, 198—206). Ch. Abs. (*p*)

Cure of anæmia by ingestion of mammalian liver. E. Lemaire (Bull. Soc. d'Encour., 1936, **135**, 330—332).—A review. H. G. R.

Anæmia in pregnancy. J. A. Boycott (Lancet, 1936, **230**, 1165—1172).—The common anæmia of pregnancy is of the hypochromic type and is due apparently to Fe deficiency. It responds to Fe treatment. L. S. T.

Hypochlorhydria in asthma with special reference to the age incidence. M. Gillespie (Quart. J. Med., 1935, **4**, 397—405).—Low free acidity of the gastric contents was present in 51% and low total acidity in 41% of 109 cases of asthma. Subacidity (74% of cases) was most marked in the age group under 15 years. After 6 months' treatment, 16 of 46 cases showed increased acid content of the juice. Nutr. Abs. (*m*)

Treatment of Basedow's disease with large doses of vitamin-*A* (Vogan). H. Wendt (Münch. med. Woch., 1935, **82**, 1160—1162).—The body gains in wt. and basal metabolism falls almost to normal. R. N. C.

Treatment of tuberculous lung-bleeding with vitamin-*C* (Cebion-Merck). F. Hasselbach (Fortschr. Therap., 1935, **11**, 407—411; Chem. Zentr., 1935, ii, 1573). R. N. C.

Treatment of gynæcological bleeding with vitamin-*C*. E. Junghans (Klin. Woch., 1935, **14**, 899). R. N. C.

Biochemical factors of cancer. M. Copisarow (Chem. and Ind., 1936, 422).—The metabolic significance of enzymes, vitamins, and hormones in cancer and the curative effect of methylene-blue, cystine disulphoxide, and vitamin-*E* treatments support the author's views on the ætiology of cancer (cf. B., 1934, 1032; 1935, 107). F. O. H.

Cancer. I. Influence of parenteral administration of certain sugars on the p_H of malignant tumours. C. Voegtlin, R. H. Fitch, H. Kahler, J. M. Johnson, and J. W. Thompson. **II. Influence of [H˙] on the reversal of proteolysis in oxygenated extracts of normal and neoplastic tissues.** M. E. Maver, J. M. Johnson, and C. Voegtlin (Nat. Inst. Health Bull., 1935, No. 164, 1—14, 29—45).—I. Administration of *d*-glucose decreased the p_H of Jensen rat sarcoma, Walker rat sarcoma, Flexner–Jobling rat carcinoma, and a spontaneous adenocarcinoma in albino mice. *d*-Fructose, *d*-mannose, and maltose, and to a smaller extent *d*-xylose, affected Jensen sarcoma and Flexner–Jobling carcinoma tissue similarly whereas *l*-arabinose, *d*-galactose, lactose, and sucrose were ineffective. The active sugars increase lactic acid in the tumours.

II. Protein synthesis in digests of both tissues reached max. at neutrality under the high $[O_2]$ used. At p_H 6·0—6·5 and 7·3—7·5 slight protein synthesis was followed by proteolysis. The cystine content of the protein increased during digestion and regained its original val. during oxidation. Protein synthesis is not due to non-enzymic oxidation of ·SH in protein cleavage products. Org. S has no sp. rôle in digestion and oxidation. Ch. Abs. (*p*)

Chemotherapy of cancer. I. Lead. J. A. Bargen, B. T. Horton, and A. E. Osterberg (Amer. J. Cancer, 1935, **23**, 762—770).—Use of colloidal Pb phosphate is described. Ch. Abs. (*p*)

Therapy of enzymes in experimental rat tumours. B. Ottenstein and S. von Pastinszky (Z. Krebsforsch., 1935, **42**, 1—8; Chem. Zentr., 1935, ii, 1563). R. N. C.

Relation of glycæmia to adrenal capsules and growth of tumours. A. H. Roffo and L. M. Correa (Bol. inst. med. exp., 1931, **8**, 132—146).—Adrenaline regulates glycæmia and stimulates growth of tumours. Ch. Abs. (*p*)

Œstrogenic hormones and mammary adenocarcinoma of the mouse. A. Lacassagne (Compt. rend. Soc. Biol., 1936, **122**, 183—184). R. N. C.

Independence of malignant growths and type of metabolism. A. Reis and L. Kluge (Arch. exp. Path. Pharm., 1936, **181**, 281—284).—Data of metabolic processes in rat sarcomata before and after general and local (growth-inhibiting) *X*-irradiation indicate their independence of growth; this is exemplified by the increase (32—48%) in uric acid content. F. O. H.

Chlorine and cholesterol metabolism of animals suffering from cancer. Hepatorenal symptom complex. S. Sümegi (Frankfurter Z. Path., 1935, **48**, 386—397).—During the growth of a transplanted rat carcinoma, cholesteryl ester in blood was low and the rise and fall in blood-Cl′ following NaCl administration was > normal. Later blood-Cl′ was greatly increased and diuresis and Cl′ excretion were reduced. These changes were accompanied by a rise in total blood-cholesterol. They are ascribed to changes in liver and kidney due to toxic degradation products of tumour-protein. Nutr. Abs. (*m*)

Tobacco and cancer. O. Schürch and A. Winterstein (Z. Krebsforsch., 1935, **42**, 76—92; Chem. Zentr., 1935, ii, 1563).—Tobacco-tar obtained from burning cigars contains 9% of nicotine, > 5% of hentriacontane, $C_{31}H_{64}$, m.p. 66°, a higher (possibly dipalmityl) ketone, m.p. 79°, a phytosterol, m.p. 135°, and about 2% of a *substance*, $C_{10}H_{14}O$, b.p. 50—55°/1 mm., which is responsible for the odour of tobacco-smoke, and is possibly a furan derivative; the odour is destroyed by catalytic hydrogenation. No product of the tar exhibits carcinogenic activity. R. N. C.

Effect of interference with the vascular supply on the induction of dibenzanthracene tumours. J. W. Orr (Brit. J. Exp. Path., 1935, **16**, 121—126).—Fibrosis of subcutaneous tissue produced by insertion and removal of linen threads accelerated tumour induction in mice by 1 : 2 : 5 : 6-dibenzanthracene. Injection of adrenaline hydrochloride further accelerated the tumours. Ephedrine sulphate had no effect. Ch. Abs. (*p*)

Effect of methylene-blue on oxygen consumption and respiratory quotient of normal and tumour tissue. J. J. Jares (Amer. J. Cancer, 1935, **24**, 80—89).—Addition of methylene-blue (I) in concns. of > 0·01% to normal and tumour tissues causes an initial increase followed by a decrease in O_2 consumption. The R.Q. of spleen, kidney, liver, and cerebral cortex are increased and that of testis and tumour tissues are lowered by (I) in final concn. of 0·01%. Injection of (I) and $CH_2Br{\cdot}CO_2H$ into rats bearing Jensen sarcoma does not affect the rate of tumour growth. Ch. Abs. (*p*)

Purine-nitrogen content of the organs of rats on various diets and suffering from avitaminosis and Jensen sarcoma. S. Edlbacher and P. Jucker (Z. physiol. Chem., 1936, **240**, 78—98).—Purine-N/total N ratios are given for liver, kidney, muscle, and spleen. *A*-Avitaminosis does not affect the vals., whilst sarcomatous rats have a high liver-purine content. F. O. H.

Natural sources of fluorine and "mottled teeth" in Maldon, Essex. J. H. Bowes and M. M. Murray (Nature, 1936, **137**, 828).—Pond-H_2O, well-H_2O, grass, and rabbit's teeth from this "mottled teeth" area contain much more F than similar substances from other localities. L. S. T.

Possible rôle of the anterior pituitary in human diabetes. O. L. V. de Wesselow and W. J. Griffiths (Lancet, 1936, **230**, 991—994).—Injection of the blood-plasma of elderly, obese, glycosuric patients into rabbits diminishes the hypoglycæmic action of insulin in a manner closely resembling that obtained with extracts of the anterior pituitary gland. The plasma of young diabetic and normal subjects produces no alteration in the blood-sugar response of the rabbit to insulin. These results are discussed in relation to the pathogenesis of human diabetes. L. S. T.

Influencing of diphtheric circulation weakness by cortical hormone and vitamin-*C*. P. Bamberger and L. Wendt (Klin. Woch., 1935, **14**, 846—847). R. N. C.

Pathogenesis of galactorrhœa : hormonal processes in physiological lactation. E. J. Kraus (Arch. Gynäkol., 1935, **159**, 380—394; Chem. Zentr., 1935, ii, 1568). R. N. C.

Treatment of gapeworm disease. P. A. Clapham (J. Helminthology, 1935, **13**, 3—8).—The eggs and adults of the parasite were killed by allyl sulphate in linseed oil (0·33 minim, 3 times daily). Ch. Abs. (*p*)

Ascorbic acid in paroxysmal hæmoglobinuria. L. Armentano (Nature, 1936, **137**, 910).—Paroxysmal hæmoglobinuria is accompanied by a marked deficiency in ascorbic acid, administration of which causes it to disappear. L. S. T.

Chronic hypoglycæmia. M. A. Goldzieher (Endocrinol., 1936, **20**, 86—92). R. N. C.

Biochemical aspects of canine hysteria treatment. J. McGhee (Vet. Rec., 1936, **16**, 416).—The condition is due to deficiency of blood-Mg rather than -Ca. R. N. C.

Relative values of urea-stibamine and neostibosan in treatment of kala-azar. C. U. Lee and C. F. Chu (Chinese Med. J., 1935, 49, 328—329).—Urea-stibamine is the more potent and also the more toxic. Ch. Abs. (*p*)

Iodine values and total lipins of leprous human blood-sera. H. H. Anderson and J. van D. Anderson (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1470—1473).—The I val. is low and total lipins (I) are high in early cuta-neural leprosy. Chaulmoogra (II) therapy increases the I val. and lowers (I), but the large amount of (II) given may be responsible for this. R. N. C.

Fat metabolism in liver disease. S. M. Leites, L. S. Lifschitz, and A. I. Odinov (Méd. exp. Ukraine, 1935, No. 1, 44—54).—In patients suffering from affections of the liver the curve of the alimentary lipæmia following a meal of 75 g. of butter and 20 g. of bread did not differ greatly from normal, but the ketones in the blood were > normal. In very severe cases the amount of ketones was reduced. Nutr. Abs. (*m*)

Blood-purine derivatives in migraine. J. Beazell and L. A. Crandall, jun. (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1450—1451).—Adeninonucleotide-N and purine-N show no deviation from the normal vals. R. N. C.

Chemistry of muscle in myopathy. R. Debré, J. Marie, and D. Nachmansohn (Compt. rend., 1936, **202**, 520—522).—In myopathy the lactic acid and glycogen contents of muscle remain within normal ranges but the proportion of P compounds is much reduced. A. G. P.

Insulin hypoglycæmia in myxœdema. A. Baudouin, E. Azérad, and J. Lewin (Compt. rend. Soc. Biol., 1936, **122**, 170—171).—The hypoglycæmia is abnormally prolonged, the abnormality disappearing on treatment with thyroid. R. N. C.

Nephritis in the dog : differential diagnosis with special reference to urine analysis. N. S. King (Vet. Rec., 1936, **16**, 445—459).—A lecture and discussion. R. N. C.

Congo-red test in nephropathics. I. E. E. Fernandez (Día Méd., 1932, 4, 681).—Retention of dye is shown especially in renal disease.
Ch. Abs. (*p*)

Paget's disease. II. Effect of adreno-cortical extract treatment on blood-phosphatase in Paget's disease. L. Berman (Endrocrinol., 1936, **20**, 226—227).—The phosphatase is reduced.
R. N. C.

Secondary pellagra. S. L. Simpson (Quart. J. Med., 1935, 4, 191—201).—Pellagra following gastrectomy was cured by vitamin-B_2. Gastrectomy may deprive the patient of an essential dietary factor which is derived from or bound up with protein. Adrenal hypofunction and pellagra are related.
Ch. Abs. (*p*)

Copper content of blood in pregnancy. S. L. Thompsett and D. F. Anderson (Brit. J. Exp. Path., 1935, **16**, 67—69).—Blood-Cu increases during the last 3 months of pregnancy and is not greatly affected by associated anæmias. Milk is deficient in Cu and Fe. In fœtal life a reserve of these metals is laid down, notably in liver, to be utilised in the period between birth and weaning. Cu feeding during pregnancy lowers the Fe content of liver and tissues and increases that in blood Cu is essential for blood formation even when excess of Fe is present.
Ch. Abs. (*p*)

Influence of pregnancy on histamine sensitivity. I. Karády and F. Stróbl (Orvosi Hct., 1935, **79**, 589—590).—Changes in sensitivity occur from the third or fourth month. Ch. Abs. (*p*)

Streptococcal complement-fixing reaction in rheumatic diseases. A. Beck and F. Coste (Brit. J. Exp. Path., 1935, **16**, 20—25).—Tuberculous and pregnancy sera frequently react with steptococcal lipin antigens; positive reaction with these occurs only in cases of rheumatic disease in which, clinically, a connexion with streptococcal infection is probable. Ch. Abs. (*p*)

Experimentally rachitic rats after injection of porphyrin. E. Emminger and B. Büchele (Virchow's Archiv, 1935, **295**, 46—56; Chem. Zentr., 1935, ii, 1395).—Porphyrin deposition in the bones is apparently unrelated to rickets. R. N. C.

Silicosis. W. E. Cook (J. Hyg., 1935, **35**, 207—218).—A review. Ch. Abs. (*p*)

Action of iodine-containing saline atmosphere on thyroid hyperplasia. H. Uffenorde (Z. ges. exp. Med., 1934, **93**, 547—569; Chem. Zentr., 1935, ii, 1570). R. N. C.

Use of nitric acid in the serological diagnosis of cattle trypanosomiasis. E. R. Jones (Vet. Rec., 1936, **16**, 602—605).—HNO_3 gives a sp. serological reaction for trypanosome infections, the reaction being a modification of the xanthoproteic reaction.
R. N. C.

Cholesterolæmia and tuberculosis. L. Llopis (Crón. med. Valenciana, 1934, **28**, No. 809).—Blood-cholesterol is unrelated to the course of pulmonary tuberculosis. Ch. Abs. (*p*)

Value of urine examination in disease of the urinary tract in the dog. J. McGhee (Vet. Rec., 1936, **16**, 570—574). R. N. C.

Metabolism of cold-blooded animals in different latitudes. H. M. Fox (Nature, 1936, **137**, 903—904).—The O_2 consumption of English marine invertebrates is $>$ that of related northern species each at the temp. of their habitat. Since locomotory activities are approx. equal, non-locomotory metabolism appears to be higher in the warmer-H_2O species. Ciliary activity parallels O_2 consumption, but in crustaceans the respiratory movements of the warmer- and colder-H_2O species are equal. L. S. T.

Effects of complete and incomplete hypophysectomy on basal metabolism of pigeons. O. Riddle, G. C. Smith, and C. S. Moran (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1614—1616).—Basal metabolism falls after both complete and incomplete hypophysectomy, to extents which are influenced by the temp. of measurement. R. N. C.

Respiratory metabolism of the seal and its adjustment to diving. L. Irving, O. M. Solandt, D. Y. Solandt, and K. C. Fisher (J. Cell. Comp. Physiol., 1935, **7**, 137—151). R. N. C.

Fumarate and tissue-respiration. I. Effect of dicarboxylic acids on oxygen consumption. G. D. Greville (Biochem. J., 1936, **30**, 877—887; cf. Annau *et al.*, A., 1935, 1406).—The effects of malonate (I) and fumarate (II) on the respiration of tissues (pigeon's breast-muscle, rat diaphragm) are the more pronounced the greater is the degree of damage which they have suffered. (I) inhibits carbohydrate respiration in rat's brain-cortex and retina and respiration, accelerated by dinitro-*o*-cresol, in brain-cortex and tumour. (II) partly counteracts the inhibition. (I) does not inhibit respiration, accelerated by brilliant-cresyl-blue, in tumour.
W. McC.

Determination of the respiratory quotient of tissues in Ringer's solution containing phosphate. E. Ciaranfi (Biochem. Z., 1936, **285**, 238—240).—The amount of preformed CO_2 in tissues $\propto$ their wt. if determined in unbuffered Ringer's solution after the const. of proportionality has been determined. The respiration of tissues is subsequently measured in a vessel described, the p_H of the solution being adjusted as required. W. McC.

Metabolism of normal and tumour tissues. XVI. Action of some oxidation–reduction systems. F. Dickens (Biochem. J., 1936, **30**, 1064—1074; cf. this vol., 629).—Thionine (I) and brilliant-cresyl-blue (II) considerably increase rat kidney oxidation in HCO_3' and PO_4''' media, whilst pyocyanine (III) produces an increase in PO_4'''–Ringer's solution. All three dyes increase the respiration of kidney in lactate medium, whilst methylene-blue has a progressive toxic action and gallocyanine is without effect. With tumour-tissue, the max. increase (200%) in respiration in glucose occurs with (I) and (II), and these also increase the oxidation of brain-tissue in glucose. Phenosafranine greatly increases aërobic glycolysis in both brain and tumour tissue. (III) increases respiration and decreases aërobic and anaërobic glycolysis of tumour. Phenazine methiodide and NN'-dimethyldihydrophenazine have similar but less marked actions. J. N. A.

Low-temperature blood meals as a source of essential amino-acids for nutritive purposes. W. C. Miller (Vet. Rec., 1936, **16**, 311—321).—A lecture and discussion. R. N. C.

Oxidative deamination of amino-acids. M. Neber (Z. physiol. Chem., 1936, **240**, 59—69).—The principal NH_2-acids are oxidatively deaminated (by the same enzyme; glycine most readily) to decreasing extents by liver, kidney, and intestinal mucosa. The isolated organs, unlike those *in situ* (as indicated by feeding experiments), deaminate the naturally-occurring optical forms more slowly than the corresponding non-natural isomerides. Deamination of tryptophan and *d*(+)-histidine by kidney occurs to only a small extent; that of alanine by liver is accompanied by disappearance of part of the resultant NH_3 which is not converted into urea, but probably utilised for purine synthesis. F. O. H.

Nutritive value of canavanine (amino-acid). M. Ogawa (J. Agric. Chem. Soc. Japan, 1936, **12**, 256—259; cf. A., 1935, 1407).—Canavanine is not essential for growth in the later part of the growing period of animals. J. N. A.

Conversion of histidine into histamine in the animal organism. W. Bloch and H. Pinösch (Z. physiol. Chem., 1936, **239**, 236—240).—The histamine (I) content (0·0015—0·0025%) of the lungs of guinea-pigs is doubled following subcutaneous injection of histidine (II) (1·0 g. per kg of body-wt.). No increase follows injection of other NH_2-acids or of 0·9% aq. NaCl, or fasting. Organs other than the lungs contain very little (I) and no definite increase in their content of (I) follows injection of (II). W. McC.

Inactivation of histamine *in vivo*. C. A. Dragstedt and F. B. Mead (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1435—1437).—Histamine injected in almost lethal doses in the dog disappears in 30—40 min.; in smaller doses the time is proportionately less. R. N. C.

Metabolism of betaine and allied tertiary nitrogenous bases in the ruminant. W. L. Davies (J. Dairy Res., 1936, **7**, 14—24).—The principal tertiary N metabolite of all *tert.* N bases examined is NMe_3O (I). Traces of NMe_3, $NHMe_2$, and NH_2Me also occur in cow's urine. The N of simple bases [NMe_3 and (I)] is rapidly and almost quantitatively excreted as (I). From 14 to 43% of the N of betaine (II), choline, and $NMe_2{\cdot}CH_2{\cdot}CO_2Me$ is excreted as (I), the rate of excretion varying with the nature and amount of the bases fed. No unchanged (II) was found in the urine. A. G. P.

Fission of proline in the animal organism. M. Neber (Z. physiol. Chem., 1936, **240**, 70—77).—Decomp. of *l*(—)-proline and -hydroxyproline by liver and kidney tissue is accompanied by formation of $\cdot NH_2$ but not of NH_3. From the products of decomp. were isolated *l*(+)-glutamic (I) and α-ketoglutaric acid (II). The decomp. of pyrrolidonecarboxylic (III) and α-amino-δ-hydroxyvaleric acid (IV) (the latter yielding δ-hydroxy-α-ketovaleric acid) indicates that the route is proline →(III)+(IV)→(I)→(II), (II) being further catabolised. F. O. H.

Tryptophan metabolism. VIII. Growth and kynurenic acid production on carboxylic acid derivatives of tryptophan. L. C. Bauguess and C. P. Berg (J. Biol. Chem., 1936, **114**, 253—257; cf. A., 1934, 1252).—*Me*, m.p. 149—150°, *Et*, m.p. 105—106°, *Pr*, m.p. 124—125°, *Ph*, m.p. 151° (decomp.), and *CH_2Ph tryptophancarboxylate*, m.p. 122—124°, were all inactive in promoting growth or kynurenic acid production in tryptophan-deficient rats. H. D.

Metabolism of sulphur. XXIII. Influence of ingestion of cystine, cysteine, and methionine on the excretion of cystine in cystinuria. H. B. Lewis, B. H. Brown, and F. R. White (J. Biol. Chem., 1936, **114**, 171—184; cf. A., 1935, 1008).—When cystine (I) isolated from urine or obtained from human hair was fed to a cystinuric, no extra (I) was excreted in the urine, but there was a large increase in urinary SO_4''. When cysteine hydrochloride was fed, there was an increase in the amounts of (I) and SO_4'' excreted. When *dl*-methionine (II) was fed, extra (I) but not SO_4'' was excreted. If the cystinuric received a high-protein diet, the extra excretion of (I) after feeding (II) was < when a moderate protein diet was fed. There was no evidence of the presence in the urine of a readily decomposed complex containing (I). J. N. A.

Metabolism of argininic acid. K. Felix and H. Müller (Z. physiol. Chem., 1936, **240**, 1—9).—Argininic acid (A., 1928, 744) is harmless to fed animals (*e.g.*, 10—30 g., daily in man, the blood-sugar being unaffected), but doses of 0·5 g. per kg. are toxic and occasionally lethal to starved animals. In animals and men suffering from muscular dystrophy (but not from myasthenia), it increases excretion of (partly newly formed) creatine, whilst in diabetics it is converted mainly into urea and sugar. F. O. H.

Comparative studies on the concentrating power of the liver and kidney with respect to cholalic acid. E. Chabrol, J. Cottet, and J. Sallet (Compt. rend. Soc. Biol., 1936, **122**, 184—186).—Slow continuous intravenous injection of cholalic acid (I) in the dog does not increase blood-(I); most of the injected (I) is removed by the liver, very little being eliminated in the urine. Increase of the rate of injection causes a rise of blood-(I) through inability of the liver to remove the increased supply; renal elimination is not increased in this case, nor if the bile duct is ligatured. In dogs poisoned with tolylenediamine, (I) is removed during injection as in normal dogs, but blood-(I) rises after injection has ceased. R. N. C.

Increase in cholalic acid in the liver and muscle during experimental cholalæmia. E. Chabrol, J. Cottet, and J. Sallet (Compt. rend. Soc. Biol., 1936, **122**, 186—188).—Cholalic acid (I) injected into normal dogs is removed by the liver but not stored in the muscles. With the bile duct ligatured, (I) is stored in both liver and muscles, their content continuing to increase after injection has ceased. In dogs intoxicated by tolylenediamine, storage of (I) is reduced in both liver and muscles.

R. N. C.

Origin and fate of urea in the developing hen's egg. J. Needham, J. Brachet, and R. K. Brown (J. Exp. Biol., 1935, 12, 321—336).—The urea produced during development of the embryo is not derived from the NH_3 of protein catabolism, or from uric acid (I) by means of uricase. Its source appears to be an arginine–arginase system present from the 2nd day of incubation onward. Arginase (II) activity falls very regularly as development proceeds, reaching a min. about the 12th day, but the quantity of activators present does not decrease. (II) occurs in the yolk sac, but in much smaller quantity than in the embryo. Results of injection of urea and tartronic acid show that Werner's urea conjugation hypothesis of (I) synthesis is untenable. Injection of $(NH_4)_2CO_3$ markedly increases the (I) content of the embryo.

Nutr. Abs. (*m*)

Pigment metabolism during and after a fifty-day period of starvation. G. G. Gasenko and N. P. Blagovestova (Folia Hæmatol., 1935, 53, 283—290).—Changes in the pigment of internal organs were slow. Urobilin excretion reached a min. $\ll$ normal. Decreased formation of red cells followed only at the end of the period and during recovery.

Ch. Abs. (*p*)

Biological degradation of chlorophyll. V. Dihydropyrophæophorbide-*a* and pyrophæophorbide-*b* from the fæces of sheep. H. Fischer and F. Stadler (Z. physiol. Chem., 1936, 239, 167—178; cf. A., 1933, 627, 1173; 1934, 317).—Probophorbide-*a* is a mixture of pyrophæophorbide-*a*. (I) and its H_2-derivative (II). (I) and (II) are partly separated by adsorption on talc. Probophorbide-*b* probably consists chiefly of methylphæophorbide-*a* or contains chlorin-c_6. In the sheep, after the Mg of chlorophyll is eliminated in the stomach, part of the phæophytin produced passes through the intestine unchanged, but most is converted into (I) and small amounts of pyrophæophorbide-*b*, together with a little phæophorbide. Enzymic hydrogenation of (I) yields (II), $CH{:}CH_2$ being reduced to Et. According to the conditions which prevail in the intestine (I) and (II) are excreted or converted into phylloerythrin.

W. McC.

Cholesterol content of different organs during digestion and fasting. K. Yamasaki (Fukuoka Acta med., 1935, 28, 106—107).—During digestion of food the cholesterol (I) content of the adrenals was increased but that of other organs remained const. In fasting animals the (I) content of the adrenals was decreased and that of the liver increased. Increased liver-(I) was noted, together with hypercholesterolæmia, after oral administration of (I).

Nutr. Abs. (*m*)

Cholesterol ratio in living and necrotic neoplastic tissue. A. H. Roffo (Bol. inst. med. exp., 1932, 9, 503—510).—Increased cholesterol occurs in neoplastic tissue.

Ch. Abs. (*p*)

Phosphorus metabolism. V. Relation between urinary phosphate and blood-phospholipin during absorption of fats. G. E. Youngburg (J. Lab. Clin. Med., 1935, 20, 920—922; cf. A., 1933, 178).—Increased blood-phospholipin (I) occurring after ingestion of a high-fat meal is not accompanied by a decrease in urinary PO_4''' (II). The P of (I) and (II) is not drawn from the same immediate source.

Ch. Abs. (*p*)

Fat metabolism. XVII. Biological degradation of hydrogen esters. I. Metabolism of ethyl hydrogen sebacate in dogs. B. Flaschenträger and K. Bernhard (Z. physiol. Chem., 1936, 240, 19—22).—Of 30 g. of Et H sebacate ingested, 91·8% is apparently metabolised and 5·2% is excreted unchanged, 2·1% as sebacic acid and 0·63% as Et H suberate. This confirms the enhanced catabolism of $(CO_2H)_2$-acids by blocking a $\cdot CO_2H$ (cf. A., 1935, 1015, 1151; Verkade and van der Lee, this vol., 234).

F. O. H.

Influence of food-fat of varying degrees of unsaturation on blood-lipins and milk-fat. L. A. Maynard, C. M. McCay, and L. L. Madsen (J. Dairy Sci., 1936, 19, 49—53).—Changes in the I val. of milk-fat appear 18—24 hr. after changes in the ration and reach max. in 2—4 days. Similar though less marked changes occur in blood-lipins.

A. G. P.

Effect of various fats in the production of dietary fatty livers. H. J. Channon and H. Wilkinson (Biochem. J., 1936, 30, 1033—1039).—Rats fed on a diet containing 5% of protein supplemented with butter or beef fat or palm, coconut, or olive oil all developed fatty livers. The differences in accumulation were accounted for by the differences in the content of glycerides, and the degree of accumulation was inversely $\propto$ the I val. of the dietary fat, and, except in the case of olive and cod-liver oils, ran parallel with the % of C_{14}—C_{18} saturated acids. The data indicate that the nature of the stored fat depends, both in the glyceride and phosphatide fraction, on that of the dietary fat.

H. D.

Effect of dietary caseinogen in the prevention of fatty livers. A. W. Beeston, H. J. Channon, J. V. Loach, and H. Wilkinson (Biochem. J., 1936, 30, 1040—1046).—1 g. of caseinogen (I) is equiv. to 7—8 mg. of choline (II) in preventing liver-fat deposition in rats receiving diets containing 40% of fat. The presence of marmite in the diet has no further effect on liver-fat accumulation than that due to its (II) content. With diets containing 5% of (I) and 40% of fat, 3 mg. of (II) per day reduced the liver-fat from 20 to 10%, but amounts varying from 8·8 to 79·8 mg. did not prevent some fat accumulation. Edestin has lipotropic action.

J. N. A.

Serum-lipin changes in relation to the intermediary metabolism of fat. A. E. Hansen, W. R. Wilson, and H. H. Williams (J. Biol. Chem., 1936, 114, 209—222).—Serum-lipins (I) were determined in dogs, which were fasted to deplete the fat depôts, and then fed a complete diet, including linseed oil or coconut oil as sources of fat. After regaining wt., the dogs were fasted for 7 days and then fed a diet in which carbohydrate replaced the fat. This was followed by a fast of 4 days. The highest vals. for total lipins were found during the ingestion of fat, and the lowest during feeding of carbohydrate, with approx. equal vals. at the end of the two fasts. The level of (I) varied with the intensity of fat metabolism. All the principal fractions of the total lipin were concerned with the transport and utilisation of fat. Dogs receiving coconut oil had higher (I) vals. than those receiving linseed oil. The difference was greatest in the neutral fat. The I vals. of the total fatty acids and, to a smaller extent, those of the phospholipin fatty acids reflected the characters of the diet during the feeding, and of the depôt fat during fasting. J. N. A.

Physiology of pyrimidines. VIII. Metabolism of *iso*barbituric acid in the rabbit. W. J. Conway and L. R. Cerecedo (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1600—1601).—Feeding with *iso*barbituric acid (I) results in a decrease of inorg. S and increases in sulphuric esters and urea; hence (I) is metabolised as in the dog and man. R. N. C.

Fate of phenol after intravenous injection in the dog. G. Barac (Compt. rend. Soc. Biol., 1936, **122**, 74—75).—PhOH diffuses into the organs, the liver and kidneys taking up slightly > the remaining organs. R. N. C.

Blood-sugar equilibrium in simultaneous portal and arterial perfusion of the liver. N. Fiessinger, H. Bénard, M. Herbain, and L. Dermer (Compt. rend. Soc. Biol., 1936, **122**, 32—33).—Liver-glycogen (I) in the dog falls considerably, particularly if initially high, whilst blood-sugar rises proportionally, falling again when (I) is exhausted. R. N. C.

Metabolism of the frog's egg in course of development. IV. Glycogen content of the egg from segmentation to hatching. J. Brachet and J. Needham (Arch. Biol., 1935, **46**, 821—825).—Glycogen (I) is steady until gastrulation, afterwards falling progressively. The % of desmoglycogen also falls. (I) is reduced by anaërobiosis at segmentation, but not at neurulation. R. N. C.

Digestion and utilisation of starch by the honey bee. R. Lotmar (Arch. Bienenk., 1935, **16**, 195—204).—Starch (I) is digested by bees and utilised almost as well as sugar. Cooked (I) is less readily digested, but intact (I) grains are not digested, being protected by amylopectin against the action of bee-diastase (II). Pollen-(I) is not attacked by pollen-(II) but by bee-(II). Nutr. Abs. (*m*)

Biochemistry and physiology of glycuronic acid. VI. Excretion of ethereal sulphate by the rabbit following administration of phenylglucosides. VII. Conjugation of borneol in man. J. Pryde and R. T. Williams (Biochem. J., 1936, **30**, 794—798, 799—800; cf. A., 1934, 442).—VI. Phenyl-α- and -β-glucosides, orally or subcutaneously administered to rabbits, are not excreted as glycuronides, but as (the equiv. amount of) Ph_2SO_4, indicating hydrolysis to PhOH and glucose.

VII. Following ingestion of borneol (2 g.), up to approx. 80% is excreted as glycuronide within 10—12 hr. F. O. H.

Effect of low-carbohydrate diet on glucose tolerance in spontaneous hypoglycæmia. B. B. Clark and J. A. Greene (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1459—1462).—Glucose tolerance is increased. R. N. C.

***In-vitro* studies on lactic acid metabolism in tissues from polyneuritic chicks.** W. C. Sherman and C. A. Elvehjem (Biochem. J., 1936, **30**, 785—793).—Determinations of O_2 uptake, lactic acid (I) removal, and reduction of methylene-blue by normal and polyneuritic chick tissues indicate that diminished O_2 uptake and removal of (I) occur in heart- but not brain-tissue, the deficiency being remedied by addition of vitamin-B_1. Inhibition of (I) dehydrogenase by $AcCO_2H$ in avitaminous heart and kidney is > that in normal tissues. The influence of -B_1 on the dehydrogenation of (I) and the bearing of the data on those of Birch and Mann (A., 1934, 705) are discussed. F. O. H.

Post-mortal formation of lactic acid in muscles of seals, ducks, and hens. J. F. Manery, M. S. Welch, and L. Irving (J. Cell. Comp. Physiol., 1935, **7**, 131—135).—The anaërobic reserves of the skeletal muscle of the seal are not different from those of other animals, nor those of the duck from those of the hen. Post-mortal formation of lactic acid is the same in muscles of hens and ducks without buffers, and is high in the pectoral muscles. The CO_2 contents of the muscles are also similar in the two species. R. N. C.

Degradation of butyric acid by surviving liver. E. Ciaranfi (Biochem. Z., 1936, **285**, 228—237).—The respiration and production of ketones by surviving guinea-pigs' liver in presence of $Pr^{a}CO_2Na$ and the ratio β-hydroxybutyric acid (I) to $CH_2Ac{\cdot}CO_2H$ (II) produced are greater when the Ringer's solution employed contains NaH_2PO_4 as buffer than when it contains $NaHCO_3$. The liver oxidises (I) slightly with production of (II), and partly reduces and partly oxidises (II), free O_2 being consumed. In Ringer's solution the reaction (I) $\rightleftharpoons$ (II) proceeds equally rapidly in both directions when $NaHCO_3$ is the buffer but (II)→(I) is more rapid when NaH_2PO_4 is buffer. Consumption of O_2 and production of CO_2 by the liver are increased by addition of $Pr^{a}CO_2Na$, indicating that degradation proceeds beyond the stage of (I) and (II). W. McC.

Variations in magnesium content of the normal white rat with growth and development. D. M. Greenberg and E. V. Tufts (J. Biol. Chem., 1936, **114**, 135—138; cf. A., 1927, 894).—The Mg content of normal rats is least in the fœtus and increases rapidly to a max. val. of 40 mg. per 100 g. at 4 weeks of age. This is followed by a const. level for 11 weeks, and a subsequent reduction of about 20%. There is no significant difference in the Mg content of the two sexes. The H_2O content progressively decreases from birth. J. N. A.

Sulphur and sulphate balance experiments with sheep. F. J. Warth and T. S. Krishnan (Indian J. Vet. Sci., 1935, **5**, 319—331).—A loss (intake less that recovered in excreta and estimated to be present in live-wt. increase and wool) of total S and SO_4'' always occurred in sheep receiving a diet low in S and in those receiving the same diet supplemented with SO_4'', but there was a gain in org. S. The org. S of the urine increased after feeding inorg. SO_4''. NUTR. ABS. (*m*)

Response of the kidney to an alkalosis during salt deficiency. R. A. McCANCE and E. M. WIDDOWSON (Proc. Roy. Soc., 1936, **120**, B, 228—239).—Overbreathing by normal persons produced alkaline urine with increased excretion of $Na^{\cdot}$ and $K^{\cdot}$ and diuresis. In salt-deficient cases, oliguria with no change in p_H or excretion of $Na^{\cdot}$ and $K^{\cdot}$, but with a generalised lowering of functional renal activity, occurred, administration of CO_2 preventing the latter. H. G. R.

Physiology of digestion in ruminants. I. Acid and enzyme content of the abomasum of the sheep. F. W. KRZYWANEK and W. BUSS (Arch. wiss. pr. Tierheilk., 1935, **69**, 321—328).—In the abomasum acidity and p_H were not closely correlated, the discrepancy being due to the presence of org. acids. In a pregnant sheep, HCl fell to a very low level 1 month before lambing and gradually rose to normal at lambing. Pepsin was the only enzyme of importance. NUTR. ABS. (*m*)

Denaturation of proteins by sound waves of audible frequencies. L. A. CHAMBERS and E. W. FLOSDORF (J. Biol. Chem., 1936, **114**, 75—83).—Ovalbumin and plastein, but not horse serum-albumin, are denatured by intense sonic vibration sufficient to produce vigorous cavitation of the solutions, except in an atm. of N_2 or H_2 or in vac. The solubility of the products equals that of the heat-denatured products. H. G. R.

Modifications of the state of oxidation–reduction of tissues *in vivo* during photo-sensitisation. P. DUBOULOZ and J. ROCHETTE (Compt. rend. Soc. Biol., 1936, **122**, 221—222).—Irradiation of the skin of the guinea-pig injected with methylene-blue decolorises it irreversibly. The skin of the frog similarly coloured is decolorised in darkness, but the colour is restored on irradiation. R. N. C.

Determination of oxidation–reduction potentials [in biological media]. L. P. DUGAL (Natural. Canad., 1936, **63**, 113—133).—Data are recorded for the survival of specimens of *Gammarus locusta* and of the larvæ of coastal plankton in media of varying p_H and r_H. H. J. E.

Oxidation–reduction potential of α-amino-ketobutyric ester and of reductone. C. MARTIUS and F. KNOOP (Z. physiol. Chem., 1936, **240**, 195—197).—The average potential, E_0, of the ester (I) at 25° and p_H 4·53—8·68 is 0·077, whilst the vals. for reductone and ascorbic acid are approx. equal. (I) readily decolorises indigotindisulphonate, Janus-green, phenosafranine, safranine VE, and (chiefly irreversibly) neutral-red. W. McC.

Effect of certain environmental conditions on skin and body temperatures and rate of oxygen consumption. H. FREEMAN (Refrig. Eng., 1935, **30**, 27—30).—Effects of temp. and R.H. are examined. CH. ABS. (*p*)

Physiological basis of the sensation of cold. IV. Influence of temperature and of thyroid extract on oxygen consumption of the anæsthetised rabbit. V. Relation between basal metabolism, regulation of temperature, and sensation of cold. J. M. O'CONNOR (Proc. Roy. Irish Acad., 1936, **43**, B, 23—33, 34—42).—IV. The influence of temp. on the basal metabolic rate in normal and in thyrotoxic rabbits is the same, the vals. at all temp. being raised 50% in the latter.

V. The onset of shivering between 22° and 38° corresponds with a change in the basal metabolic rate with temp. H. G. R.

Effects of fractional doses of prolan and *X*-rays in association on the morphology of the ovary of the adult rabbit. P. DESAIVE (Arch. Biol., 1935, **46**, 669—694). R. N. C.

Interpretation of the action of *X*-rays and prolan on the ovary of the adult rabbit. P. DESAIVE (Arch. Biol., 1935, **46**, 695—715). R. N. C.

Exogastrulation in amphibia after *X*-ray exposure. W. C. CURTIS, J. A. CAMERON, and K. O. MILLS (Science, 1936, **83**, 354). L. S. T.

Absorption of radium emanation by the human body through the skin. R. WAGNER (Sitzungsber. Akad. Wiss. Wien, II, A, 1934, **143**, 521—531).—Rn from radioactive baths is absorbed through the skin and lungs, the latter being the more important route. The permeability of the skin to Rn is about 0·01%, but is increased with large skin surface and excessive hypodermal fat tissue. Absorption in warm H_2O baths is > in ordinary air-baths. R. N. C.

Electromotive force in biological systems. IV. Effect of various nitrogen–oxygen and carbon monoxide–oxygen mixtures on the electromotive force and oxygen consumption of frog skin. A. B. TAYLOR (J. Cell. Comp. Physiol., 1935, **7**, 1—21).—$[O_2]$ of $< 20\%$ in N_2–O_2 mixtures lower both E and O_2 consumption, the fall of E being > that of O_2 consumption, which ∝ the $[O_2]$. Pure O_2 stimulates E and increases O_2 consumption slightly. The decline of E and of respiration in CO–O_2 mixtures depends partly on the [CO], the fall of E being the greater in certain limits. Complete recovery after treatment with either mixture depends on the time of exposure and the composition of the mixture. The effect of CO is unaffected by light. R. N. C.

Ionic antagonism in the water-permeability of sea-urchin eggs. T. R. FUKUDA (J. Cell. Comp. Physiol., 1935, **7**, 301—312).—The rate of swelling of the eggs in hypotonic solutions depends on the ionic composition of the solution. The permeability changes caused by two-salt mixtures containing chlorides of bivalent cations are simple if both cations are bivalent, but more complicated if one only is bivalent; the changes are characteristic of the mixed ratio. $Na^{\cdot}$–$Ca^{\cdot\cdot}$ mixtures show max. at 99·5% and 50% $Na^{\cdot}$, and min. at 5% and 100% $Ca^{\cdot\cdot}$; $Na^{\cdot}$–$Mg^{\cdot\cdot}$ mixtures show max. at 30% and 75% $Na^{\cdot}$ and a min. at 100% $Mg^{\cdot\cdot}$. R. N. C.

Permeability of the egg of *Arbacia punctulata* to certain solutes and water. D. R. STEWART and M. H. JACOBS (J. Cell. Comp. Physiol., 1936, **7**, 333—350).—The permeability consts. for a no. of glycols and H_2O are given. They are doubled after fertilisation of the egg. $CaCl_2$ in the solution decreases the permeability of the cell to H_2O, but does not affect that to glycol. R. N. C.

Distribution of penetrating ammonium salts between cells and their surroundings. M. H. Jacobs and D. R. Stewart (J. Cell. Comp. Physiol., 1936, 7, 351—365).—The rate of penetration of cells by NH_4 salts of weak acids is > that by salts of strong acids, the mechanism probably being by means of the hydrolysis products. The *Arbacia* egg does not swell in isotonic NH_4Cl or hypertonic $KCl–NH_4OAc$ mixture, but ultimately swells in hypertonic $NH_4Cl–NH_4OAc$ mixture; swelling is caused in NH_4Cl by addition of NaOAc, but not by Na_3BO_3, although the cell is apparently permeable to $(NH_4)_3BO_3$. This suggests that in a mixture of a penetrating and a non-penetrating NH_4 salt the former may distribute itself so as to raise the internal concn. above the equilibrium concn., but that sufficiently weak acids may prevent this increase. R. N. C.

Phosphocreatine and lactic acid changes in potassium chloride contractions of frog's muscle in acid solution. S. R. Tipton (J. Cell. Comp. Physiol., 1936, 7, 433—443).—Muscles in solution buffered at p_H 6·0 are contracted by 0·04% of K. The contraction is accompanied by a sudden rise in O_2 consumption, and by hydrolysis of phosphocreatine (I), but lactic acid (II) does not begin to accumulate until [K] reaches 0·08%. At this concn. (I) resynthesis is increased. Anaërobic (I) hydrolysis with high [K] is > aërobic hydrolysis. In presence of O_2 (I) is resynthesised even if (II) formation is not increased. R. N. C.

Effect of cations on the velocity of the extinguishing action of animal and vegetable organs. G. Russo (Boll. Soc. ital. Biol. sperim., 1935, 10, 805—807).—The velocity of extinction in the presence of cations in the alkaline p_H zone decreases in the order $Li^{\cdot}>K^{\cdot}>Na^{\cdot}>Sr^{\cdot\cdot}>Mg^{\cdot\cdot}$, $Ba^{\cdot\cdot}>Ca^{\cdot\cdot}>NH_4^{\cdot}$, whilst in the acid zone it increases in the order $K^{\cdot}<Ba^{\cdot\cdot}<Ca^{\cdot\cdot}<Sr^{\cdot\cdot}<Mg^{\cdot\cdot}<Na^{\cdot}$, $NH_4^{\cdot}<Li^{\cdot}$. R. N. C.

Effect of inorganic salts on the diuretic action of salyrgan. C. B. Ethridge, D. W. Myers, and M. N. Fulton (Arch. Int. Med., 1936, 57, 714—728).—Diuresis is increased by the addition of salts which produce acidosis and diminished by those producing alkalosis. H. G. R.

Inorganic salts in nutrition. Changes in kidneys of rats fed a diet poor in inorganic constituents. P. P. Swanson, C. A. Storvick, and A. H. Smith (J. Biol. Chem., 1936, 114, 309—319).—Rats on a salt-deficient diet showed enlarged kidneys for 45 days, followed by a regression in kidney size. The proportions of ash, Ca, and P did not decrease, and at the end of 3 weeks the $[Ca^{\cdot\cdot}]$ was abnormally high. H. D.

Influence of arsenic on basal metabolism, blood-residual nitrogen, and reticulocytes in man. E. Knell (Arch. exp. Path. Pharm., 1936, 181, 292—300).—Administration of single therapeutic doses of org. or inorg. As preps. lowers the basal metabolism and blood-residual N (I), the latter subsequently increasing and, with inorg. As, exceeding normal vals. Prolonged dosage increases (I) and the reticulocyte count, the course of the latter together with those of hæmoglobin and erythrocytes resembling (and hence indicating the non-specificity of) those due to anti-anæmic preps. F. O. H.

Value of carbon dioxide in counteracting oxygen lack. E. Gellhorn (Nature, 1936, 137, 700—701).—The presence of 3% of CO_2 in the air prevents or alleviates the effect of a low $[O_2]$ (8—9%) on brain-stem reflexes in the rabbit and on vision, muscular co-ordination, and mental processes in man. L. S. T.

Mineral metabolism. XXXIII. Iodine in the nutrition of sheep. II. A. I. Malan, P. J. Du Toit, and J. W. Groenewald (Onderstepoort J. Vet. Sci., 1935, 5, 189—200).—There was no significant difference in wt. or wool production between merino ewes receiving KI daily and those receiving none. Nutr. Abs. (*m*)

Action of lithium on sea-urchin development. J. Runnström (Biol. Bull., 1935, 68, 378—384).—Effects of $Li^{\cdot}$, to which the eggs are very sensitive, are described. Pyocyanine counteracts the action of Li which affects the structure of the protoplasm and respiration. Ch. Abs. (*p*)

Effect of uranium nitrate on insulin hypoglycæmia and glycolysis in the blood. R. Weekers (Compt. rend. Soc. Biol., 1936, 122, 78—80).—$UO_2(NO_3)_2$ does not appreciably modify the reduction of blood-sugar and $-PO_4$ caused by insulin, but it slackens, without inhibiting, blood-glycolysis. R. N. C.

Effect of sulphur on the bone-marrow. A. H. Müller (Klin. Woch., 1935, 14, 917—918).—Stimulation of the bone-marrow by thioalbin (I) is not more productive than that by S-free proteins. Pure S and inorg. S compounds do not affect blood-formation. The action of (I) on the hæmopoietic system is due probably to the presence of Fe and Cu as impurities. The effect of Cu on the marrow is not strengthened by S. R. N. C.

Effect of dietary supplements of different forms of sulphur on the wool of merino sheep. C. M. van Wyk, M. L. Botha, and J. G. Bekker (Onderstepoort J. Vet. Sci., 1935, 5, 177—188).—The daily supplements were: 0·45 g. of cystine, 0·7 g. of a mixture of sulphates, 0·36 g. of KCNS, 5·0 g. of S, and 0·12 g. of S. They had no effect on grease wt., clean wt. and % yield of fleece, mean length, thickness, and fibre wt. Nutr. Abs. (*m*)

Dipolar theory of sense of odour. A. Muller (Perf. Essent. Oil Rec., 1936, 27, 202—205).—An attempt to explain the odour of organic compounds in relation to their structure by consideration of the theory of dipole moments. P. G. M.

(A) Second ecolysis of the infective larvæ of certain *Trichostrongylidæ* in solutions of sodium sulphide and of organic compounds containing sulphur. (B) Behaviour of sterilised exsheathed infective Trichostrongylid larvæ in sterile media resembling their environment in ovine hosts. G. Lapage (J. Helminthol., 1935, 13, 103—114, 115—128).—(A) Effects of garlic, Na_2S, cysteine, sulphonal, and $Na_2S_2O_3$ are compared. NaOCl was more toxic than these.

(B) The larvæ had a wide p_H tolerance (3·6—9·6). In media containing sheep serum the longevity of the larvæ was not affected by lactose, fructose, glucose, vitamins, or NH_2-acids. Yeast and liver extracts were toxic. CH. ABS. (*p*)

Blood-chloride and the renal secretion of urea in mice. P. FEYEL (Compt. rend., 1936, **202**, 507—509).—Increased secretion of urea (I) in the brush-bordered cells following intraperitoneal injection of (I) is accompanied by increased secretion of Cl'. Similarly, injection of NaCl leads to increased secretion of both (I) and Cl'. A. G. P.

Influence of dietary factors on renal secretion of urea in mice. P. FEYEL (Compt. rend., 1936, **202**, 687—689).—Interrelationships between urea and Cl excretion are further examined (cf. preceding abstract). A. G. P.

Influence of renal secretion of urea on the functioning of the chloride resorption mechanism in the mouse. P. FEYEL (Compt. rend., 1936, **202**, 871—874).—The special cells of the Schweigger–Seidel segment of the kidney of a mouse after a meat diet for 15 days contained more Cl' than those of a similar mouse which had received an injection of urea just before examination. The renal secretion of urea is accompanied both by secretion and resorption of Cl'. J. N. A.

Physiological effects of certain aliphatic thiocyanates on the isolated heart preparation from the roach, *Blatta orientalis*. J. F. YEAGER, A. HAGER, and J. M. STRALEY (Ann. Entom. Soc. Amer., 1935, **28**, 256—264).—Thiocyanates are grouped in three classes according to their action in inhibiting the contraction rate of the heart prep.: (i) Me and Et, (ii) Pr^α, Pr^β, and Bu, (iii) trimethylene, "butylcarbitol," and diethylene glycol thiocyanates, ββ′-dithiocyanodiethyl ether, and diethylene glycol dithiocyanoacetate. Relative activity of the groups is (iii)>(ii)>(i). CH. ABS. (*p*)

Pharmacological action and pathological effects of alkyl thiocyanates in relation to chemical constitution and physical-chemical properties. W. F. VON OETTINGEN, W. C. HUEPER, and W. DEICHMANN-GRUEBLER (J. Ind. Hyg., 1936, **18**, 310—336).—Of 8 alkyl thiocyanates studied the lower homologues (Me, Et, etc.) cause stimulation and subsequent paralysis of the medullary centres following subcutaneous injection, whilst octyl and decyl thiocyanate are active only in very large doses, and lauryl and myristyl thiocyanate are almost inactive. The higher homologues irritate the mucous membrane. P. G. M.

Action of acetone and of ketones present in diabetic blood on the heart. M. M. BAGOURY (Brit. J. Exp. Path., 1935, **16**, 25—33).—Toxicity of $CH_2Ac\cdot CO_2H$ is > that of $COMe_2$. β-Hydroxybutyric acid $(\ngtr 1\%)$ has no effect on the heart, its action being attributed to the changes in acid–base equilibrium in the blood. Administration of glucose and of insulin does not modify the action of the three substances. CH. ABS. (*p*)

Action of methylglyoxal on acetoacetic acid. VI. Liver- and muscle-glycogen after feeding of the ketol and simultaneous injection of insulin. R. STÖHR (Z. physiol. Chem., 1936, **240**, 23—25; cf. A., 1935, 1412).—Glycogen (I) formation from $CH_2Ac\cdot CO_2H$ (II) in the liver of starving rats is inhibited by insulin (III). Compensatory (I) formation in muscle does not occur, the level being diminished. Parallel results with AcCHO indicate that (II) is degraded into two 3-C compounds (AcCHO?). (II) does not inhibit (III)-hypoglycæmia. F. O. H.

Physiological behaviour of trioses and related compounds. VI. Liver- and muscle-glycogen after feeding of methylglyoxal and simultaneous injection of insulin. R. STÖHR (Z. physiol. Chem., 1936, **240**, 26—28; cf. A., 1934, 919).—See preceding abstract. F. O. H.

Fat and calcium metabolism. II. Effect of tributyrin on the excretion of calcium by the intestine in the growing rat. A. WESTERLUND (Lantbruks-Högskolans Ann., 1933—1934, **1**, 21—31; Chem. Zentr., 1935, ii, 1574).—Tributyrin does not affect Ca excretion. R. N. C.

Increased cardiac output [after administration of dinitrophenol]. J. V. GALGIANI and M. L. TAINTER (J. Pharm. Exp. Ther., 1936, **56**, 451—463).—The increased O_2 consumption of dogs *injected* with the drug is only partly due to increased cardiac output. H. D.

Sensitising action of antioxygenic phenols after post-gangliary enervation of the nictitating membrane. Z. M. BACQ (Compt. rend. Soc. Biol., 1936, **122**, 112—114).—The sensitising action is inhibited by antioxygenic phenols and aminophenols, but not by non-phenolic antioxygens or amines. The action takes place in the tissues. R. N. C.

Characterisation of the sympathomimetic and parasympathomimetic substances in the blood by dialysis *in vivo*. J. GAUTRELET, D. BROUN, H. SCHEINER, and E. CORTEGGIANI (Compt. rend., 1936, **202**, 1302—1304).—The parasympathomimetic action of carotid or jugular blood is due to the presence of acetylcholine and the sympathomimetic action of the adrenal vein blood to adrenaline. H. G. R.

Inhibition of autoxidation of adrenaline by the aqueous humour. F. BONHOMME (Compt. rend. Soc. Biol., 1936, **122**, 110—112).—The inhibition is feebler than that exerted by plasma; the inhibiting agents are proteins and ascorbic acid. R. N. C.

Choline as a factor in the elaboration of adrenaline. R. L. STEHLE, J. I. MELVILLE, and F. K. OLDHAM (J. Pharm. Exp. Ther., 1936, **56**, 473—481).—A possible genetic relationship between choline (I) and adrenaline (II) is investigated by determining the effects on the blood pressure of possible intermediates in the synthesis of (II) from (I). *Methyl*-β-*acetoxyethylammonium chloride*, m.p. 105°, and β-3 : 4-*dihydroxyphenyldimethyl*-β-*hydroxyethylammonium iodide*, m.p. 186°, are described. H. D.

Comparative action of sodium oleate and ricinoleate on lecithin. G. Vallette (Compt. rend. Soc. Biol., 1936, **122**, 150—152).—Na ricinoleate clarifies lecithin suspensions at p_H 7·0—9·0, the clarifying power increasing with p_H. Na oleate only clarifies the suspension at $p_H > 9·8$. R. N. C.

Dephosphorylation processes during phloridzin diabetes in the dog. A. Lambrechts (Compt. rend. Soc. Biol., 1936, **122**, 72—73).—There is no evidence of inhibition by phloridzin of the action of phosphatases. R. N. C.

Pharmacodynamics of dyes with distinct electrical charges. A. H. Roffo and R. L. Ramirez (Bol. inst. med. exp., 1931, **8**, 99—104).—The action of electro-positive dyes (malachite-green, neutral-red, methylene-blue) on blood pressure and respiration is not appreciably modified by admixture with electro-negative dyes (acid-fuchsin, phenolsulphonephthalein). Ch. Abs. (*p*)

Toxic action of percutaneously-applied irradiated wool-fat preparations in the sense of hypervitaminosis-*D*. M. Schieblich and G. Pallaske (Deut. med. Woch., 1935, **61**, 957—960).—Crude wool-fat, lanolin, and eucerin do not generate vitamin-*D* when irradiated with ultra-violet light, nor do they after irradiation cause calcification of the inner organs when rubbed on the dorsal skin of guinea-pigs. R. N. C.

Methæmoglobin test for the determination of anti-anæmic efficiency of liver-extracts. J. F. Wilkinson and W. Deutsch (Klin. Woch., 1935, **14**, 926—928; Chem. Zentr., 1935, ii, 1586).—The methæmoglobin test is no real indication of the anti-anæmic efficiency and cannot replace clinical methods. H. N. R.

Ornitho-callicrein. I. E. Werle and J. Hürter (Biochem. Z., 1936, **285**, 175—191).—Callicrein (I), injected into birds (hen, goose, pigeon, duck), has no effect on the blood pressure, but the fæces and pancreas of birds contain *ornitho-callicrein* (II) which closely resembles (I), having a powerful reducing effect on the blood pressure of birds, but none on that of mammals. (II) is inactivated by heat, *N*-HCl, *N*-NaOH, I, H_2O_2, and the serum of birds and mammals.. In the fæces of birds (II) is accompanied by small amounts of a substance, probably histamine. W. McC.

Effect of adrenal and splanchnic denervation on sugar tolerance of dogs. G. De Takáts and F. P. Cuthbert (Arch. Surg., 1935, **30**, 150—161).—The sugar tolerance increased under both conditions. Dogs are more responsive to insulin and less to the hyperglycæmic action of adrenaline. Bilateral vagotomy does not diminish the increased sugar tolerance obtained in these operations. Interruption of the sympathico-adrenal mechanism may cause increased storage or fixation of glycogen in the liver. Ch. Abs. (*p*)

Fixation of alcohol on the encephalon of rats with experimental alkalosis. J. Lévy (Compt. rend., 1936, **202**, 440—441).—The min. anæsthetic dose of EtOH for normal rats is sufficient for rats with alkalosis produced by NaOH, but insufficient for those with alkalosis produced by Na_2CO_3. The hyposensitivity to EtOH of the latter is discussed. H. G. M.

Blood-alcohol and its relation to intoxication in man. R. G. Turner (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1548—1552).—Blood-EtOH must be $> 0·2\%$ to cause noticeable intoxication; 0·31—0·4% causes marked intoxication, 0·41—0·5% stupor, and $> 0·5\%$ coma or death. R. N. C.

Specific dynamic action and toxicity of synthetic alcohol and fermentation alcohol. J. Křiženecký and F. Diakov (Z. Unters. Lebensm., 1936, **71**, 149—159).—No important difference was observed, but the synthetic EtOH appeared to contain an impurity with narcotic properties. E. C. S.

Activity of anæsthetics and their partition in blood. N. Lazarev (Compt. rend. Acad. Sci., U.R.S.S., 1936, **1**, 237—238).—In the blood of frogs and mammals those anæsthetics which are most powerful exist almost entirely "bound," whilst those which are weak exist chiefly in aq. solution. Probably the hæmoglobin shares in binding the anæsthetics. W. McC.

General narcosis with gases, *cyclo*propane, carbon dioxide, nitrous oxide, ethylene, and oxygen. A. Chueco (Semana méd., 1935, I, 1793—1799). Ch. Abs. (*p*)

Summation of the action of two soporifics on molecular combination. H. J. Fuchs (Arch. exp. Path. Pharm., 1936, **181**, 215—218).—Mol. combinations of diethylbarbituric acid (I) and bromo*iso*valerylcarbamide have a soporific action >, and a toxicity <, that of (I). F. O. H.

Sodium propylmethylcarbinylallylbarbiturate, a short-acting hypnotic. E. E. Swanson (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1563—1565). R. N. C.

Effects of phenacetin and aspirin, respectively, on action of phenobarbital. A. Gilman and H. G. Barbour (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1634—1636). R. N. C.

Cinchophen (atophan) therapy and the liver. T. Brugsch (Semana méd., 1935, I, 1907—1910).—Cinchophen mobilises uric acid, reduces inflammation, and stimulates hepatic secretion. Ch. Abs. (*p*)

Ocular reactions due to arsphenamine. J. J. Skirball and F. M. Thurman (Amer. J. Syphilis, 1935, **19**, 197—209).—Substitution of I', Bi, or Hg for arsphenamine does not affect the return of the eye condition to normal. Ch. Abs. (*p*)

Purgative constituent of castor oil. G. Valette and R. Salvanet (Compt. rend. Soc. Biol., 1936, **122**, 68—70).—Ricinoleic acid prepared by way of the Li salt exerts a purgative action, but not that prepared by way of the Et ester and saponification with LiOH. R. N. C.

Pharmacological actions of indolyl-*N*-methylharmine. I. Bakhsh (Quart. J. Pharm., 1936, **9**, 37—47; cf. Gunn, A., 1912, ii, 857).—The min. lethal dose of indolyl-*N*-methylharmine hydrochloride (I) per kg. by subcutaneous injection is 0·11 (frog), 0·038 (guinea-pig), and 0·1 g. (mouse). Toxic doses cause a descending paralysis of the central nervous system. Small doses increase whilst large doses diminish blood pressure. (I) dilates the coronary vessels in the isolated rabbit's heart. Conc. solutions cause contraction of frog's skeletal muscle, whilst smooth muscle is first stimulated. (I) kills *Paramecium caudatum* and *Amœba proteus* in concn. of 1 in 320,000 and 1 in 1,280,000, respectively, in 24 hr. Judged by toxicity (I) is approx. three times as active as harmine. J. N. A.

Relative values of caffeine and hypertonic glucose and saline solutions in reducing cerebrospinal fluid pressure. A. Blau (Arch. Int. Med., 1936, **57**, 749—757).—Reductions obtained on intravenous injection of hypertonic aq. glucose or caffeine–NaOBz were inconsistent and transient, whereas those with 15% saline were uniform and more persistent. H. G. R.

Pharmacology of caffeine and of tea and coffee. G. R. Lynch (Analyst, 1936, **61**, 300—302).—The action of caffeine on the central nervous system, muscular tissue, and kidney is discussed. E. C. S.

[Pharmacology of] twenty-three quaternary ammonium iodides. H. M. Lee, A. M. VanArendonk, and K. K. Chen (J. Pharm. Exp. Ther., 1936, **56**, 466—472).—The nicotine- and muscarine-like activities of the compounds are compared. d-, m.p. 206·5—207°, and dl-*Methylephedrine methiodide*, m.p. 230—230·5°, d-, m.p. 212—213°, l-, m.p. 211—212°, and dl-*methyl-ψ-ephedrine methiodide*, m.p. 168·5—169°, β-*hydroxy*-β-*phenyl*iso*propyl-dimethylethyl-*, m.p. 166—167°, and -*benzyldimethyl-ammonium iodide*, m.p. 188—189°, β-*hydroxy*-β-*phenyl*-α-*ethyl-*, m.p. 162—163°, and β-1 : 2-*diethoxyphenyl-ethyltrimethylammonium iodides*, m.p. 245°, *dendrobine methiodide*, m.p. 246°, *tetrandrine dimethiodide*, m.p. 273°, 4-β-*ethoxyethyl-*, m.p. 93—95°, and 4-β-*acetoxyethyl-morpholine methiodide*, m.p. 123·5—124·5°, are described. H. D.

Absorption of drugs through the oral mucosa. II. III. Fat–water solubility coefficient of alkaloids. R. P. Walton (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1486—1488, 1488—1492).—III. Absorption of drugs with high oil–H_2O solubility coeffs. is > of those with relatively low coeffs. R. N. C.

[Pharmacology of] morphine, codeine, and their derivatives. XII. Isomerides of morphine and dihydromorphine. N. B. Eddy (J. Pharm. Exp. Ther., 1936, **56**, 421—431 ; cf. A., 1936, 517).—The pharmacological activities of α-, β-, and γ-*iso*morphine and of their H_2-derivatives were compared among themselves and with those of analogous codeine derivatives. H. D.

Pharmacology and therapeutics of curare and its constituents. R. West (Proc. Roy. Soc. Med., 1935, **28**, 565—578).—Fractionation of the active constituents is described. Tubocurarine and curine are examined. Ch. Abs. (*p*)

Eupaverine in relation to papaverine and visammin. K. Samaan (Quart. J. Pharm., 1936, **9**, 23—36).—Eupaverine (I) and papaverine (II), injected intravenously into dogs, have a min. lethal dose of 60 and 40 mg. per kg., respectively. In the toad, rabbit, and dog, (I) depresses the heart and relaxes all types of smooth muscle by direct action on the muscle fibres, but the degree of action varies greatly. The relative actions of (I), (II), and visammin of antagonising the effect of $Ba^{\cdot\cdot}$ vary with different types of plain muscle. The low toxicity of (I) compared with (II) is offset by its insolubility. J. N. A.

Analgesic and respiratory action of the morphine group. W. Keil and F. H. Pöhls (Arch. exp. Path. Pharm., 1936, **181**, 285—291).—The course and extent of analgesic and respiratory action (the latter being produced by smaller doses than is the former) of morphine alkaloids (I) in rabbits were determined. Morphinised animals have a diminished sensitivity to (I). F. O. H.

Emetic action of lobelanine and lobelanidine. A. Clementi (Arch. exp. Path. Pharm., 1936, **181**, 265—272).—Toxicity and emetic and respiratory action were determined in dogs, rabbits, and frogs. F. O. H.

Respiratory stimulating action of lobeline and carbon dioxide on the morphinised respiratory centre in rabbits. B. Behrens and W. Graubner (Deut. med. Woch., 1934, **60**, 1675—1677). R. N. C.

Relation between nicotine and the sexual hormone I. Lethal dose of nicotine and sexual difference. II. Effect of castration and sexual hormone on nicotine activity. III. Effect of nicotine on morphological and histological changes of female sex organs after injections of female sexual hormones. IV. Antidotal action of luteohormone on nicotine toxicity during anaphylaxis. (A) Effect of nicotine on blood-sugar, blood pressure, and anaphylaxis. (B) Effect of luteohormone on anaphylaxis. (C) Effect of nicotine with luteohormone on anaphylaxis. V. Discussion and conclusion. Y. C. Lee (J. Severance Union Med. Coll., 1935, **2**, 80—86, 87—107, 108—127, 128—155, 156—159).—The greater resistance of female animals to the action of nicotine is due to the production of luteohormone. Ch. Abs. (*p*)

Rôle of glycæmic response to nicotine. Tobacco smoking and blood-sugar. W. J. McCormick (Amer. J. Hyg., 1935, **22**, 214—220).—Injection of adrenaline into rabbits prior to administration of nicotine reduces the toxic action of the latter. Hyperglycæmia caused by smoking is a protective response and results in decreased potential muscular energy, through lowering the body-reserve of glycogen. Ch. Abs. (*p*)

Determination of the average lethal dose in the biological assay of digitalis by the frog method. K. O. Moller (Quart. J. Pharm., 1936, **9**, 7—22).—A method by which the average lethal dose (LD 50) can be determined on 30—40 frogs (kept at a const. temp.) by means of a mortality curve is described. The statistical determination of LD 50 is discussed. " Summer frogs " are much more resistant to digitalis than " winter frogs." J. N. A.

Antagonistic effect of iodides in baldness and toxicity due to thallium acetate. O. V. Hykeš and F. A. Diakov (Nature, 1936, **137**, 871).—In addition to KI (cf. A., 1935, 1533), LiI, NaI, and MgI_2 largely counteract the toxic effects in rats due to TlOAc. L. S. T.

Influence of diet on the toxicity of mercurochrome and of neoarsphenamine. R. Wien (Quart. J. Pharm., 1936, **9**, 48—59; cf. Burn and Elphick, B., 1930, 881).—The sensitivity of mice towards mercurochrome and neoarsphenamine varies with different diets which, however, have no influence on liver-glycogen. J. N. A.

Ability of rats to discriminate between diets of varying degrees of toxicity. K. W. Franke and V. R. Potter (Science, 1936, **83**, 330—332).—Rats are able to detect and differentiate between small quantities of Se in foodstuffs. Sub-lethal injections of Na_2SeO_3 cause a voluntary starvation even when normal diets are offered. L. S. T.

Toxic wheat grown on soils containing selenium.—See B., 1936, 515.

Toxicity of carbon tetrachloride; animal exposures and field studies. H. F. Smyth, H. F. Smyth, jun., and C. P. Carpenter (J. Ind. Hyg., 1936, **18**, 277—298).—100 p.p.m. of CCl_4 vapour are safe for continuous daily exposure of workmen. At a level of 50—400 p.p.m., damaged liver and kidney cells regenerate with increased resistance. P. G. M.

Toxicity and potential dangers of phenylhydrazine zinc chloride. W. F. von Oettingen, W. Deichmann-Gruebler, and W. C. Hueper (J. Ind. Hyg., 1936, **18**, 301—309).—This double salt is less toxic than $NHPh{\cdot}NH_2$ (I) as judged by subcutaneous injection in rats; the min. lethal dose is 0·25 mg. as opposed to 0·18 mg. per g. and its effect is more prolonged. Unlike (I), it does not evolve toxic vapours when heated to 100—170°. It destroys red cells and reduces the hæmoglobin content of the blood, but to a smaller degree than (I). It produces more pronounced skin irritation than (I). P. G. M.

Influence of diet on toxicity of ethylhydrocupreine hydrochloride. A. J. Nedzel (J. Lab. Clin. Med., 1935, **20**, 944—945).—Rabbits fed exclusively on oats are more, and those on a diet of carrots less, sensitive to ethylhydrocupreine than are those on a mixed diet. Differences are attributed to variations in acid/base ratio resulting from the diets. Ch. Abs. (*p*)

Chronic poisoning by aniline. Acute poisoning by *p*-phenylenediamine. A. Buzzo, R. Carratalá, and C. Martinez (Rev. crim. psychiat. méd. legal, 1931, **18**, 427—433).—Cases are described. Methods of detecting p-$C_6H_4(NH_2)_2$ are given. Ch. Abs. (*p*)

Hypoglycæmia as a result of agaric (*Amanita phalloides*) poisoning. L. Binet and J. Marek (Compt. rend., 1936, **202**, 1219—1220).—Aq. extracts, subcutaneously (10 mg. per kg.) or orally administered to dogs, cause a marked hypoglycæmia and uræmia followed by death in several hr. Rabbits show convulsions, and the liver is rendered glycogen-free. Extracts of non-toxic agarics do not produce these effects. J. L. D.

Snake venom. F. Micheel and F. Jung (Z. physiol. Chem., 1936, **239**, 217—230).—The dried venom of *Naja flava* when purified by ultrafiltration, dialysis, and fractional pptn. with $COMe_2$ at the isoelectric point (p_H about 7·0) yields an extremely active ($0{\cdot}12\times10^{-6}$ g. is min. lethal dose per g. for mice) neurotoxin (I), mol. wt. 2500—4000, containing C, H, O, N, S, and combined mineral matter. (I) is stable at p_H 2—8, especially if glycerol is present, but is inactivated by O_2 and reactivated by cysteine at p_H 2—3. (I), which is related to the proteins, probably contains a thiolactone group, but no free ·SH. The venom also contains a poison having about 12% of the activity of (I). The poison from the venom of vipers *Crotalus adamanteus*, *C. terrificus*, *Bothrops jararaca*, and *Ancistrodon piscivorus* also contains S, has mol. wt. ⩾ that of (I), and is more sensitive to attack by acid and alkali. Its stability is greatest at p_H 5·8—6·0. In the venom it is accompanied by a dialysable activator. Albumin, albumose, and (in greater amount) peptone also activate the poison to the same extent. W. McC.

Ascorbic acid oxidase from drumstick, *Moringa pterygosperma*. M. Shrinivasan (Current Sci., 1935, **4**, 407—408).—Drumstick press juice contains an enzyme system (prep. described) which is capable of oxidising ascorbic acid (I) and is inactivated when boiled or treated with $CCl_3{\cdot}CO_2H$ (cf. Szent-Györgi's hexoxidase; A., 1931, 533). The oxidation of (I) occurs best at p_H 5·3 and 37°, and is unimol.; the rate ∝ the quantity of enzyme and is independent of (I) concn. The reaction is inhibited by CN′ and H_2S (0·001*M*). Guaiacum, pyrocatechol, pyrogallol, and p-$C_6H_4(NH_2)_2$ are not oxidised except in presence of H_2O_2. EtOH and $COMe_2$ destroy the (I)-oxidising constituent, but leave the peroxidase unaffected. The conclusions of Tauber *et al.* (A., 1935, 1023) concerning the existence of a sp. enzyme capable of oxidising (I) are thus confirmed. H. G. M.

Mechanism of oxidation processes. XLIV. Dehydrogenating enzyme system of *Acetobacter peroxydans*. I. H. Wieland and H. J. Pistor (Annalen, 1936, **522**, 116—137).—EtOH (0·11—0·67*M*) is dehydrogenated to MeCHO and a little AcOH by *A. peroxydans* (I) in O_2 at p_H 4·5—7 (reaction is retarded considerably at higher p_H); CO_2 is not produced. Reaction with 0·05*M*-EtOH is almost completely inhibited by KCN (*M*/4000—*M*/8000) and H_2O_2 (*M*/160—*M*/230; *M*/800 has little effect) and retarded by NaN_3 (*M*/2000—*M*/4000) and CN·ONa (*M*/5000—*M*/10000). Little conversion of MeCHO into AcOH occurs in N_2, indicating absence of mutase. H_2O_2 formed during dehydrogenation could not be detected. Since EtOH is also dehydrogenated by (I)+H_2O_2 in N_2 or air, and (I) is free from catalase, the H_2O_2 formed is probably used immediately in the respiratory process. When suspensions of (I) are shaken with H_2 a small amount is absorbed; subsequent addition of H_2O_2 (*M*/270) causes rapid consumption of the H_2 until all H_2O_2 has disappeared, but the residue is still able to effect aërobic dehydrogenation of EtOH. The enzyme system prob-

ably contains peroxidase and dehydrogenase. The organism contains cytochrome but no porphyrins.
H. B.

Amino-acid dehydrogenase. I. Proline dehydrogenase. N. B. Das (Biochem. J., 1936, 30, 1080—1087).—A purified dehydrogenase from pig's kidney oxidises *dl*-proline more readily than *d*-alanine, *dl*-phenylalanine, or leucine. Codehydrogenases I and II, flavin-enzyme, glutathione, adenyl pyrophosphate, and ascorbic acid do not activate the dehydrogenase. When the enzyme solution is heated at 80° at $p_{\rm H}$ 8 for 5 min. and then added to the original enzyme prep., there is an activation of the oxidation of proline. J. N. A.

Liver enzymes. VI. Citric acid dehydrogenase. L. Reichel and A. Neeff (Z. physiol. Chem., 1936, 240, 163—178; cf. A., 1935, 1162; this vol., 242).—The dehydrogenase (I) is purified by fractional pptn. with $COMe_2$ and with $COMe_2$–Et_2O–light petroleum (3 : 1 : 1). Adsorption on kaolin and Al_2O_3 followed by elution is not advantageous but electrodialysis is satisfactory. The activity, which is measured, after removal of protein with p-$C_6H_4Me{\cdot}SO_3H$, by determination of residual citric acid as Ca salt, is optimal at $p_{\rm H}$ 7·6 (pptn. and inactivation at 3·4) with 0·0033*M*-substrate, the max. effect being attained in 3 hr. (I) acts in presence and absence of O_2. No activity is lost on dialysis and addition of cozymase is without effect, a coenzyme being probably not required. W. McC.

Oxidase-like action of certain complex metal salts.—See this vol., 805.

Flavins and metabolism. I. Flavins and amylolysis. A. J. Charit. **II. Flavins and proteolysis.** A. J. Charit and N. V. Chaustov (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 215—218, 219—224).—I. Lactoflavin and a flavin-containing liver extract exert no influence on amylolysis by diastase or salivary amylase outside the cell, when used alone or in presence of Fe salts or aspartic acid.

II. The oxidised form of flavin under aërobic conditions does not activate the digestion of proteins by trypsin, the action of papain, or the autolytic process of muscle-tissue. H. G. M.

Free and bound amylase of barley. K. Myrbäck and S. Myrbäck (Biochem. Z., 1936, 285, 282—289; cf. this vol., 245).—In general, the liberation of bound amylase (I) in barley is caused only by proteolytic enzymes and is increased by substances (*e.g.*, HCN) which activate these enzymes. Prolonged action of papain (II) on ungerminated barley does not cause destruction of (I). Probably the β-amylase of barley exists partly free and partly bound, the action of (II) consisting in liberating more (I) not in activation. W. McC.

Hydrolysis of starch by vegetable amylases. I. K. Myrbäck (Biochem. Z., 1936, 285, 290—293).—Starch (I), oxidised with I, is hydrolysed by α- (II) and β-amylase (III) to the same extent as is untreated (I). Malt-amylase (IV) has a more powerful action than have (II) and (III), the action of (II) being slight. Dextrin obtained from (I) by the action of (III) is very slightly affected by (III), is first rapidly (up to 30% hydrolysis), then slowly attacked by (IV), and is rapidly and extensively attacked by (II). Hence (III) leaves unattacked a component of (I) which is hydrolysed by (II). W. McC.

Effect of acetylcholine hydrochloride on the amylolytic activity of pancreatin. F. Caujolle and R. Monnet (Compt. rend. Soc. Biol., 1936, 121, 1570—1572).—The activity of pancreatic amylase *in vitro* is increased. R. N. C.

Malt diastases. II.—See B., 1936, 565.

Emulsin. XXVI. Action of osmium tetroxide on sweet almond-emulsin. B. Helferich and F. Vorsatz (Z. physiol. Chem., 1936, 239, 241—256; cf. A., 1935, 783; this vol., 243).—The β-glucosidase (1 unit) of the emulsin (I) is inactivated by OsO_4 (25 mg.), the effect not being due to oxidation, which proceeds much more slowly. Aq. H_2S and cysteine (II) (1 mol. for each equiv. of active O from OsO_4 has max. effect) if added before oxidation has gone far restore much of the activity. Probably (II) acts by reducing OsO_4, and no inactivation occurs if (II) and OsO_4 are mixed before adding to (I). The action of OsO_4 is not affected by *l*-proline, indole, and *d*-alanine, but *l*-histidine and ascorbic acid have a slight protective effect. Tryptophan (approx. $\propto$ its amount) intensifies the action of OsO_4, the effect being partly counteracted by H_2S and (II).
W. McC.

Liberation of the zymase system from the yeast cell by autolysis. R. Nilsson and F. Alm (Z. physiol. Chem., 1936, 239, 179—187).—The zymase (I) is extracted partly from fresh and almost completely from dried brewer's yeast by shaking with H_2O if the extraction is preceded by a sufficiently long period of autolysis. No (I) is liberated by plasmolysis with sugar or glycerol. W. McC

Activator of zymohexase. E. Bauer (Z. physiol. Chem., 1936, 239, V; cf. Meyerhof *et al.*, A., 1934, 927).—The activator occurs in dialysed muscle extract. Thermodynamic equilibrium in the reaction hexosediphosphoric acid $\rightleftharpoons$ 2 dihydroxyacetonephosphoric acid is not attained with dil. solutions of zymohexase chiefly because of the absence of the activator. W. McC.

Nature of cozymase. K. Myrbäck (Svensk Kem. Tidskr., 1936, 48, 100—103; cf. A., 1935, 1278).—The behaviours of cozymase (I), ouabain, and Δ^{β}-angelicalactone towards oxidising agents indicate that (I) contains a lactone ring, probably 6-membered with two double linkings.
M. H. M. A.

Cozymase as a phosphate carrier. R. Vestin (Z. physiol. Chem., 1936, 240, 99—112).—In dialysed extract of rat's muscle, cozymase (I) and (I) inactivated by heat hydrolyse phosphopyruvic acid (II) and phosphocreatine and act as phosphate carriers in the transfer of PO_4 from (II) to creatine. Heat-inactivated (I) is usually more effective than (I), and is sometimes as effective as adenylic or adenosinetriphosphoric acid. W. McC.

Chemistry of highly purified cozymase. H. von Euler, H. Albers, and F. Schlenk (Z. physiol. Chem., 1936, 240, 113—126).—Methods of purification are described. The products of acid-hydrolysis include adenine, nicotinamide, and a pentose-phosphoric acid which together constitute about 60% of the purest material. Cozymase is a dibasic acid each mol. of which takes up 6 I from alkaline solution. W. McC.

Inhibition of glycolysis by heavy metals. Re-activation by Warburg's co-enzyme and Euler's cozymase. T. Wagner-Jauregg and H. W. Rzeppa (Z. physiol. Chem., 1936, **240**, I—IV).—Low concns. of Cu, Fe$^{\cdot\cdot}$, and Fe$^{\cdot\cdot\cdot}$ (but not Zn or Cd) inhibit production of lactic acid (I) from hexose-phosphoric acid in dialysed frog's muscle extract containing $MgCl_2$ and adenosine triphosphate (II). Warburg's co-enzyme (III) and Euler's cozymase (IV) (75 mol. to 1 of metal) counteract the effect, the amount of (I) then produced being $>$ double that produced with (II) and (III) or (II) and (IV) alone. Cysteine and glutathione counteract much less effectively than do (III) and (IV), whilst adenylic acid from muscle and KCN are inactive. W. McC.

Mechanism of cerebral glycolysis. F. P. Mazza and C. Malaguzzi-Valeri (Boll. Soc. ital. Biol. sperim., 1935, **10**, 725—727).—Brain extract induces the four reactions of the Embden–Meyerhof glycolysis cycle, and, like muscle extract, contains zymohexase and a dialysable co-enzyme, apparently the same as that of muscle. F′ inhibits breakdown of phosphoglyceric acid (I); it does not interfere with formation of lactic acid (II) from α-glycerophosphoric acid (III) and $AcCO_2H$ (IV), but inhibits liberation of H_3PO_4. $CH_2I\cdot CO_2H$ partly inhibits formation of (II) from (I) and (III), or from (IV) and (III), but does not inhibit breakdown of (I). R. N. C.

Control of the enzymic action of lipase. R. Itoh (Nature, 1936, **137**, 783).—A *substance* (I), m.p. 130°, $[\alpha]^{18}_{D}$ −77°, which controls the reversible action of lipase, has been isolated from *Ricinus* seed. The EtOH solution exhibits blue-violet fluorescence and two absorption bands with max. at 314 and 285 mμ. The Liebermann–Burchardt sterol reaction, the Cuboni reaction for œstrogenic hormone, and the vanillin–H_3PO_4 reaction for bile acid are positive, but the Salkowski reaction for sterol and the Gregory reaction for bile acid are negative. The reduced form of (I) activates the hydrolysis of fat by the *Ricinus* lipase and inhibits the synthesis from glycerol and oleic acid. The oxidised form acts in the reverse manner. L. S. T.

Castor bean lipase and its activator. E. Takamiya (Proc. Imp. Acad. Tokyo, 1936, **12**, 73—74).—From castor seeds have been isolated (*a*) a highly active lipase giving no reactions with Molisch, biuret, and sterol reagents but an active Millon test, and (*b*) an activator (I) in the form of needles. The enzyme catalyses both the synthesis and the hydrolysis of oils. (I) has a moderate effect on both processes, but after air oxidation it has an increased action on the synthetic but not on the hydrolytic process. After oxidation with H_2O_2 (I) strongly retards both processes. W. O. K.

Rôle of bile acids in the enzymic synthesis of cholesterol. S. V. Nedsvedski (Z. physiol. Chem., 1936, **239**, 165—166; cf. A., 1935, 1416).—In absence of salts of bile acids, pancreatic lipase (in H_2O) is destroyed in 24 hr. When Na glycocholate is added, the lipase remains almost unaltered for $\nless$ 10 days. W. McC.

Glyoxalase and its co-enzyme. II. Kidney-glyoxalase. K. Nagaya, S. Yamazoye, and S. Nakamura (J. Biochem. Japan, 1936, **23**, 41—56).—The difference between kidney- and other tissue-glyoxalases is due to an inhibitory substance (I) in kidney tissue. The inhibition occurs after reaction of (I) with glutathione (II), the reaction product combining with AcCHO at the same rate as does free (II), the respective final products being differentiated by only that from free (II)–AcCHO decomp. with glyoxalase to give lactic acid and (II). F. O. H.

Enzymic hydrolysis of acetylcholine by serum. E. Kahane and J. Lévy (Compt. rend., 1936, **202**, 781—783).—The "activity" (defined) of serum is const. when there is $<$ 5% of serum in a 0·18—1·8% solution of acetylcholine chloride; it decreases with p_H, is zero at p_H 6, and increases with rise of temp. to 38°. Serum is inactivated at 70° and by pptn. (EtOH, $COMe_2$) of the proteins: dialysates and ultra-filtrates are inactive. J. L. D.

Variations of the proteolytic activity of kinase-activated pancreatic juice as a function of the quantity of kinase. M. Guillaumie (Compt. rend. Soc. Biol., 1936, **122**, 51—53).—The quantity T of trypsin produced by a quantity x of kinase is given by $T = 70x^{0\cdot49}$. R. N. C.

Enzymic histochemistry. XIII. Distribution of enzymes in the stomach of pigs as a function of its histological structure. K. Linderstrøm-Lang, H. Holter, and A. S. Ohlsen (Compt. rend. Trav. Lab. Carlsberg, 1935, **20**, No. 11, 66—127).—The enzyme contents of the different portions of the stomach, and curves of the variation of the enzyme content with the distance below the inner surface, are given. HCl is found chiefly in the parietal cells of the fundus at 0·5 mm. depth, pepsin in the chief cells at 2 mm., peptidase in the chief cells of the stomach and the cylinder and Brunner cells of the duodenum, and esterase in the epithelial cells and interstitial tissues. R. N. C.

Digestive enzymes in cephalopods. C. Romijn (Acta Brev. neerl. Physiol., 1935, **5**, 14—15; Chem. Zentr., 1935, ii, 1385—1386).—The salivary glands of *Sepia officinalis* contain no digestive enzymes. The combined digestive juices of the liver and pancreas at p_H 5·4 contain amylase, tributyrinesterase, proteinase, carboxy- and amino-polypeptidases, and dipeptidase, but no disaccharase, and cannot hydrolyse castor oil. The pancreatic but not the liver-protease requires activation by enterokinase, which can be replaced by extract of the cæcum walls, but not by glutathione or H_2S. The enzymes show optimum activity at neutral or weakly acid p_H. R. N. C.

Phosphatases. I. Reaction mechanism of phosphatase from bone. M. Lora y Tamayo and F. Segovia. **II. New preparation of a phosphatase from bone.** M. Lora y Tamayo and J. R. Blanco (Anal. Fís. Quím., 1936, **34**, 363—375, 376—382).—I. The rate of hydrolysis at 38° of Na β-glycerophosphate (I) by phosphatase (II) isolated by the method of Martland *et al.* (A., 1929, 603) from the bones of a young rabbit $\propto$ the sq. root of the time and the sq. root of the concn. of (II). Optimum conditions are 0·05M solution, at 40°, and p_H 9·7. Ultra-violet irradiation slightly retards the hydrolysis. The optimum p_H for the hydrolysis of Na α-glycerophosphate is the same for (I).

II. Agitation of the bones of young rabbits with aq. EtOH containing EtOAc and PhMe yields a new phosphatase more active than (II). F. R. G.

Accelerant effect of α-amino-acids on the activity of bone-phosphatase. O. Bodansky (J. Biol. Chem., 1936, **114**, 273—288).—Low concns. of α-NH_2-acids prevent the rapid diminution of the rate of hydrolysis of Na β-glycerophosphate by bone phosphatase (I); the optimal concns. differ for the various acids. Mg$^{\cdot\cdot}$ has a similar influence, but also increases the initial rate of hydrolysis. With optimal concns. of Mg$^{\cdot\cdot}$ and glycine (II) the reaction velocity $\propto$ (I) concn. (II) retards the inactivation of (I) at room temp. H. D.

Serum-phosphatase in normal young rabbits. P. D. Rosahn (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1601—1603).—Between 15 and 71 days serum-phosphatase falls linearly with increasing age and wt. R. N. C.

Separation of α-glycerophosphatase and pyrophosphatase from bottom yeast. E. Bauer (Z. physiol. Chem., 1936, **239**, 195—206; cf. this vol., 380). The phosphatases of bottom yeast contain 10 times as much pyrophosphatase (I) as α-glycerophosphatase (II). (I) and (II) differ as regards effect of [H$^{\cdot}$], substrate concn., and activation by Mg$^{\cdot\cdot}$. (II) is freed from (I) by adsorption on Al_2O_3 at p_H 8·6. W. McC.

Kinetics of cell respiration. I. Rate of oxygen consumption by *Saccharomyces Wanching* as a function of p_H. P. S. Tang (J. Cell. Comp. Physiol., 1936, **7**, 475—493).—The effect of p_H varies with the buffer employed. O_2 consumption falls logarithmically in the OAc′ buffers, but less rapidly in the PO_4''' and phthalate buffers until a limiting [H$^{\cdot}$] is reached beyond which O_2 consumption falls steeply to zero. In BO_3''' buffer, respiration falls linearly from p_H 7·7 to 8·9, then increasing to 9·8. The difference of the effects of p_H in the acid and alkaline ranges suggests the existence of two different respiratory systems in the yeast cells. Respiration is inhibited at high [H$^{\cdot}$] and partly restored on returning to low [H$^{\cdot}$] after an induction period depending on the magnitude of [H$^{\cdot}$] and the time of exposure. R. N. C.

Selective fermentation. III. Fermentation of hexose–pentose mixtures. H. Sobotka, M. Holzman, and M. Reiner (Biochem. J., 1936, **30**, 933—940).—Fermentation by brewer's yeast of glucose and to a greater extent of fructose is retarded in the presence of xylose and to a smaller extent of arabinose, the effect being observed in all sugar concns. tested (0·8—6·7%) and with yeast concns. from 0·16 to 15·0% under aërobic and anaërobic conditions. The effect ran parallel with the ratio of the concns. of pentose to hexose, leading sometimes to almost complete suppression of fermentation. The fermentation, although slower, proceeds further, the total CO_2 evolved being often greater. Competitive diffusion of these sugars into the yeast cell is the major factor in the mechanism of this effect. Studies of diffusion permit the differentiation of extracellular, intracellular, and chemically bound H_2O in yeast. P. W. C.

β-Alanine and "bios." R. J. Williams and E. Rohrman (J. Amer. Chem. Soc., 1936, **58**, 695).—The growth of various yeasts (Wildiers; "Gebrüder Mayer"; Lash Miller; "Rasse M") on a medium containing inositol (5 mg. per litre) in addition to sugar and salts, is stimulated by β-alanine (I) (10^{-6} g. per 12 c.c. of culture; with 10^{-10} g. inhibition is often found); "old process" yeast responds similarly but requires vitamin-B_1 as a necessary supplement. (I) is effective only in the absence of asparagine. H. B.

Influence of crystalline hormones on the growth of certain yeasts. A. P. Weber (Compt. rend., 1936, **202**, 517—519).—*Rhodotorula suganii* and *R. glutinis* var. *Sailoi* are stimulated by folliculin and dihydrofolliculin benzoate and inhibited by heteroauxin. Six other yeasts examined were unaffected by either substance. A. G. P.

Pharmacological and therapeutic action of fresh yeast. I. Effect on blood-indican. II. Effect on blood-sugar. U. Sammartino (Arch. Farm. sperim., 1936, **61**, 13—23, 24—33).—I. Fresh Fleischmann's yeast diminishes blood-indican *in* digestive or entero-hepatic disorders, previous dieting not affecting the result.

II. Oral administration of yeast gradually reduces the hyperglycæmia occurring during skin disease etc. R. N. C.

Inhibition of the Pasteur effect. K. C. Dixon (Nature, 1936, **137**, 742).—A discussion. L. S. T.

Mechanism of enzyme action. XIII. Phosphorylation and alcoholic fermentation of sugars. Biochemistry of *Fusarium lini*, B. I. F. F. Nord, E. Dammann, and H. Hofstetter [with V. Senftner and E. Rosdorff] (Biochem. Z., 1936, **285**, 241—269; cf. A., 1933, 982).—In the fermentation of pentoses and hexoses and in the dehydrogenation of alcohols by *F. lini* (living and dried) inorg. P begins to disappear usually 2—5 days after the action and CO_2 is liberated. *F. lini* ferments *d*-xylose (no phosphorylation occurring) and *d*-arabinose. In the absence of inorg. P fermentation is slight, but reaches rates comparable with those of yeast fermentation on addition of inorg. P. No phosphorylation occurs. Accompanying morphological changes indicate that P is involved in rebuilding and buffering the cells. W. McC.

Alleged necessity for initial phosphorylation in alcoholic carbohydrate degradation. F. F. Nord, E. Dammann, and H. Hofstetter (Naturwiss., 1936, **24**, 297).—The fermentation of hexoses and pentoses by both living and dried *Fusarium lini*, B., is not necessarily preceded (although it may be accompanied) by esterification of inorg. PO_4'''. W. O. K.

Rôle of formic acid in the biochemical formation of oxalic acid. B. S. Butkevitsch and L. K.

Osnizkaja (Compt. rend. Acad. Sci. U.R.S.S., 1936, **1**, 361—364).—Proof that the $H_2C_2O_4$ (I) produced by moulds is derived from the mycelium (A., 1934, 1263) is given by the following observations. The amount of (I) formed by films of *A. niger* at 30° is not affected by varying the [HCO_2Na] in the solution, and only slightly by replacing this salt completely by $NaHCO_3$. In 6% Na_2HPO_4 solution (I) accumulates rapidly at first, but ceases after 2—3 days in the case of 2 day-old films, and after 5 days with films 3 days old, the accumulated (I) amounting to 70% of the loss in wt. of the mycelium. Such exhausted films no longer produce (I) in 1% HCO_2Na or 1·23% $NaHCO_3$, but readily do so (without change in wt.) from 2% NaOAc. J. W. B.

Metabolism of *Aspergillus niger*. I. Effect of phytin on the metabolism. W. Braun and A. Frey (Biochem. Z., 1936, **285**, 219—227).—The wt. of the mycelium and the amount of sugar consumed by *A. niger* increase with increasing inorg. and org. P [KH_2PO_4 and phytin (I) with 20% of P] content of the medium. Very small amounts of P suffice for max. production of acid by *A. niger*, the P being completely utilised. Acid production varies with the form in which N is given, decreasing with increasing supply of P if the N supply is partly org., but the form in which the N is given has less effect than has that in which P is given. Unconsumed (I) is for the most part hydrolysed by phytase which passes into the solution. When (I) is supplied the P consumption is always > that when inorg. P is given. W. McC.

Citric acid fermentation. I. Carbon balance. P. A. Wells, A. J. Moyer, and O. E. May (J. Amer. Chem. Soc., 1936, **58**, 555—558).—A C-balance for a strain of *A. niger* grown on a medium containing glucose (I) as the sole source of C is prepared; the final distribution of the C is given. The ratio wt. of citric acid (II) : wt. of CO_2 produced is $\gg$ that required by a process involving the breakdown of (I) in a manner analogous to that occurring in alcoholic fermentation. The wt. yields of (II) are also $\gg$ the max. obtainable by any process involving decarboxylation of $AcCO_2H$ as one stage (cf. Bernhauer *et al.*, A., 1932, 1168); Emde's mechanism (A., 1935, 407) is similarly excluded. H. B.

Production of kojic acid from xylose by *Aspergillus flavus*. H. N. Barham and B. L. Smits (Ind. Eng. Chem., 1936, **28**, 567—570).—The fermentation of xylose (I) by *A. flavus* was carried out over 4 years, with only moderate change in kojic acid (II) production. Using a medium containing (I), NH_4NO_3, KH_2PO_4, and $MgSO_4$, yields of > 20% of (II) were obtained. The effect of variation of PO_4''', NH_4NO_3, (I), and Mg concns. and of p_H are investigated. Fe and Ca usually inhibit and Zn has no effect on the fermentation. P. W. C.

Chemistry of mould tissue. XI. Isolation of leucine and *iso*leucine from *Aspergillus sydowi*. D. W. Woolley and W. H. Peterson (J. Biol. Chem., 1936, **114**, 85—90).—Leucine and *iso*leucine [*p-toluenesulphonate*, m.p. 124° (corr.)] have been obtained by extraction of the dried, defatted mycelium with $COMe_2$. H. G. R.

Fungicidal power of phenol derivatives. II. Strength in presence of proteins. G. J. Woodward, L. B. Kingery, and R. J. Williams (J. Lab. Clin. Med., 1935, **20**, 950—953; cf. A., 1935, 409).—Activity of many fungicides in aq. or broth suspensions is lowered by the presence of proteins. The action of I, BzOH, $Na_2S_2O_3$, salicylic acid, hexylresorcinol, and chlorothymol is reduced or inhibited by vesicle fluid, blood-serum, or hide powder. Thymol is active in presence of hide powder, but is inhibited by serum or vesicle fluid. NaOCl retains its activity in high concns. of proteins. Ch. Abs. (*p*)

Composition of plankton. I. Plankton from the Ekaterininski pond at Detskoie Selo. A. Vinogradov (Trav. lab. biogéochim. Acad. Sci. U.R.S.S., **1**, 33—48).—Analyses are given. Ch. Abs. (*p*)

Growth curves of *Polytoma uvella*: effect of oxygenation. P. B. Rottier (Compt. rend. Soc. Biol., 1936, **122**, 65—68).—The rate of growth is increased by oxygenation. R. N. C.

Action of various organic antimony compounds on *Schistosoma japonicum in vitro*. C. M. Lee and H. L. Chung (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1400—1403).—Sb^{III} compounds are more effective than Sb^{V}, and tartar emetic than Fouadin. R. N. C.

Action of chemotherapeutics on the trypanosome cell. E. Singer (Z. Hyg., 1936, **117**, 752—756). R. N. C.

Effect of ethylurethane on bacterial respiration and luminescence. G. W. Taylor (J. Cell. Comp. Physiol., 1936, **7**, 409—415). R. N. C.

Variability in the activity of bacterial enzymes. I. Effect of age of culture. W. R. Wooldridge, R. Knox, and V. Glass (Biochem. J., 1936, **30**, 926—931).—The dehydrogenase activity of many bacterial cells varies considerably with the period between inoculation and reaping of the organism, increasing at first and subsequently decreasing. The max. activity usually occurs within the first 24 hr. of growth but it could not be definitely correlated with the logarithmic phase of growth. P. W. C.

Oxidation–reduction potentials of some non-sporulating obligate anaërobes. G. M. Dack and W. Burrows (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1441—1443).—The E_h curve shows only moderate falls, never reaching −300 mv.; it rises directly lysis begins. R. N. C.

Relation between respiration and the growth of aërobic bacteria. J. Hirsch (Rev. Fac. Sci. Univ. Istanbul, 1936, **1**, 44—60).—During the linear phase of growth of aërobic bacteria the O_2 uptake $\propto$ the increasing bacterial concn. in the culture. During the following period of diminishing growth the O_2 consumption, after reaching a max., decreases and finally becomes const. at a very low val. during the stationary phase. The increase of O_2 consumption associated with growth may be made the basis of a manometric method of measuring growth rates. W. O. K.

Effect of electrolytes added to growth medium on electrophoretic potential of *Esch. coli*. G. W.

PEARCE, M. W. LISSE, and R. P. TITTSLER (Proc. Soc. Exp. Biol. Med., 1935, 32, 1572—1573).—The migration velocity is slightly reduced by $CaCl_2$, increased by Na_2SO_4, and scarcely affected by NaCl, $AlCl_3$, or Na_3PO_4. Adjustment of the initial p_H over the range 6·8±1·9 does not alter the electrophoretic velocity of organisms by > 2·5%. R. N. C.

Isolation of the growth factor of pathogenic bacteria. S. HOSOYA, Y. KUWASHIMA, S. KAYO, M. ODA, and K. KAGABE (Proc. Imp. Acad. Tokyo, 1936, 12, 67—69).—From a commercial syrupy condensed extract of the fish, scomber, a non-hygroscopic grey-white granular substance has been separated which stimulates the growth of *Staphylococcus aureus* and *B. botulinus* on a medium containing alkali hydrolysate of peptone or gelatin, arginine, cysteine hydrochloride, glucose, and salts. Other substances were obtained which acted on *S. aureus* only. W. O. K.

Microbial variants of *B. aërtrycke* and possible variation in the chemical constitution of its complete somatic antigen. M. CIUCA, L. MESROBEANU, and G. BADENSKI (Compt. rend., 1936, 202, 1314—1316).—On macerating a culture with its metabolic products, a variant obtained yields an antigen serologically identical, but with a different stability in H_2O. H. G. R.

Dehydrogenase of the *S* and *R* forms of *B. coli*. E. SORU (Compt. rend. Soc. Biol., 1936, 121, 1647—1649).—When acting as H donator, the rate of decolorisation of methylene-blue by the *S* form is > that by the *R* form. R. N. C.

Hæmotoxins in gas gangrene. J. CELAREK and S. STETKIEWICZ (Compt. rend. Soc. Biol., 1936, 122, 143—144).—Toxins of *B. perfringens* and *B. œdematiens* purified by pptn. with $(NH_4)_2SO_4$ or adsorption from $COMe_2$ with BzOH are less toxic to animals than in the crude state; the hæmolytic titre is unchanged. Adsorption with BzOH gives better yields of both toxins and hæmolysins than pptn. with $(NH_4)_2SO_4$. R. N. C.

Immuno-chemistry. I. Preparation and properties of a specific polysaccharide from *B. dysenteriæ*, Shiga. W. T. J. MORGAN (Biochem. J., 1936, 30, 909—925).—A modified method is described for the isolation from the "smooth" form of *B. dysenteriæ*, Shiga, and purification of a sp. *polysaccharide* (I) which accounts completely for the serological specificity of the organism and has the following properties: $[\alpha]_D$ +98°, N 1·61%, mol. wt. calc. from NaOI titre 5100, yields 97% of reducing sugars on acid hydrolysis with complete loss of sp. immunological properties, acid equiv. about 9000, negative orcinol, phloroglucinol, naphthoresorcinol, and protein tests, *Ac*, $[\alpha]_D^{18}$ +71°, and *Bz* derivative, $[\alpha]_D^{16}$ +63°, from both which the original (I) can be regenerated. The N of (I) does not react with HNO_2 and is therefore probably present as substituted NH_2. (I) contains 5% of Ac, isolated after acid hydrolysis as AcOAg, and this and the N content both fit the requirements of a basic unit consisting of 4 mol. of hexose with 1 mol. of acetamidohexose (II), such unit appearing from the I reduction to be repeated 6 times in the (I) mol. Colour reactions are used to follow quantitatively the liberation of (II) during acid hydrolysis and the subsequent deacetylation and these indicate that the whole of the N in the hydrolysis products is present as aminohexose. The crude (I) contains, in addition to (I), agar-like *polysaccharides*, (*a*) $[\alpha]_D$ −60°, N 5·2%, (*b*) $[\alpha]_D$ +20°, N 0·6%, which react with anti-agar bodies of immune horse serum, a *polysaccharide*, $[\alpha]_D$ +195°, identified as glycogen and a *substance*, $[\alpha]_D$ −78°, N 14·1%, sol. in 96% AcOH. P. W. C.

Analysis of the hydrophile colloids in *B. paratyphosus* colonies. L. BIRCH-HIRSCHFELD (Z. Hyg., 1935, 117, 626—634).—The mucous growth on the colonies is due to a sol. colloidal substance containing acid groups but no N, that can be hydrolysed to 40% of glucose (I) and other weakly- or non-reducing substances. It forms a stable viscous solution in H_2O. Cultures grown at 37° contain small quantities of another hydrophile substance, which can be hydrolysed to a N-rich protein, and a polysaccharide giving 80% of (I) by further hydrolysis. R. N. C.

Cultural studies in the *Salmonella* group, with particular reference to organic acids. F. KAUFFMANN and F. A. BURÓN (Z. Hyg., 1935, 117, 650—661).—The organisms fall into distinctive fermentative types according to their action on tartrate, citrate, and mucate. R. N. C.

Staphylococcal leucocidin (Neisser–Wechsberg type) and antileucocidin. J. WRIGHT (Lancet, 1936, 230, 1002—1004).—A modification of the Neisser–Wechsberg technique for the determination of these substances is described. Their relationship to hæmolysin and antihæmolysin has also been investigated. L. S. T.

Medium for production of staphylococcal toxins. G. RAMON, A. BERTHELOT, and G. AMOUREUX (Compt. rend., 1936, 202, 515—516).—Preps. from veal-broth cultures have high toxicity and antigenic activity. A. G. P.

Bacteriophage phenomena in cultures of lactic *Streptococci*. H. R. WHITEHEAD and G. A. COX (J. Dairy Res., 1936, 7, 55—62).—The isolation of bacteriophages from "starter" cultures is described. Aëration stimulates development of the phage. A. G. P.

Bacterial flora of foremilk and of rennet extract with special reference to acid proteolytic types. N. R. KNOWLES (J. Dairy Res., 1936, 7, 63—74).—Proteolytic cocci are more abundant in old than in fresh rennet samples or in foremilk. These strains probably contribute to the final breakdown of protein degradation products in ripening cheese. A. G. P.

A lactobacillus from Californian wine: *Lactobacillus hilgardii*. H. C. DOUGLAS and W. V. CRUESS (Food Res., 1936, 1, 113—119).—The organism, isolated from > 20 samples of dry, red and white wines, ferments glucose, fructose, and xylose with production of acid (mainly lactic and AcOH) but not of gas. The optimum temp. of growth is 31—37°, death occurring within 1 min. at 63°. The max. tolerated [EtOH] is 18%. E. C. S.

Optical properties of fermentation lactic acid. III. Action of inactive lactic acid-producing organisms on optically active lactic acids added to fermentation liquids. H. KATAGIRI and K. KITAHARA (J. Agric. Chem. Soc. Japan, 1936, 12, 281—283; cf. this vol., 247).—Differences in rates of racemisation of *d*- and *l*-lactic acids by *Lactobacillus plantarum* and *L. pentoaceticus* are examined.
A. G. P.

Biology of *B. cellulosae dissolvens*. Y. KHOUVINE and K. SOETERS (Compt. rend. Soc. Biol., 1936, 122, 59—61).
R. N. C.

Enzyme formation and polysaccharide synthesis by bacteria. II. A. CARRUTHERS and E. A. COOPER (Biochem. J., 1936, 30, 1001—1009; cf. A., 1935, 1419).—*B. lactis* synthesises a fructosan polysaccharide from sucrose (I) only. When *Leuconostoc dextranicum* is incubated with (I) the resulting solution, after removal of the formed dextran (II), contained fructose, yet incubation with glucose alone gave little or no (II). Small quantities of EtOH extracts of molasses accelerate growth and (II) formation; this effect is not explained by the added N. The large-scale prep. of (II) from 20% (I) is described.
H. D.

Curve of production of glyoxalines related to histamine in some bacterial cultures. M. LOEPER, L. DUCHON, A. LESURE, and A. THOMAS (Compt. rend. Soc. Biol., 1936, 121, 1591—1593).—Glyoxaline production by *B. pyocyaneus* (particularly young cultures) and *B. putrificus* is high; it is lower by *B. typhosus*, and almost negative by *B. coli*. It reaches a max. in the first few weeks, afterwards falling; proteins at the same time fall to a steady min. val.
R. N. C.

Occurrence of sterols in bacteria. R. H. SIFFERD and R. J. ANDERSON (Z. physiol. Chem., 1936, 239, 270—272; cf. Hecht, A., 1935, 663).—The unsaponifiable part of the fat of *Azotobacter chroococcum* yielded a mixture (0·13% of the fat), m.p. 156—158°, $[\alpha]_D$ −16° in $CHCl_3$, of sterols. The properties of the mixture resembled those of ergosterol rather than those of the usual animal and vegetable sterols.
W. McC.

Oxidation of amino-acids by *Bacillus pyocyaneus* (*Pseudomonas aeruginosa*). M. D. WEBSTER and F. BERNHEIM (J. Biol. Chem., 1936, 114, 265—271).—The NH_2-acids studied fell into three classes: (*a*) leucine, *iso*leucine, and histidine, only the natural isomerides of which were attacked; (*b*) phenylalanine and valine, of which non-natural isomerides increased the O_2-uptake of the bacteria without undergoing de-amination, whilst the natural isomerides were attacked; (*c*) alanine, serine, tyrosine, and proline, both isomerides of which were rapidly attacked. 0·005*M*-KCN inhibited oxidation and de-amination, whilst 1% NaF or urethane was without influence.
H. D.

Lipins of tubercle bacilli. XLIV. Comparative study of lipins of human tubercle bacillus. J. A. CROWDER, F. H. STODOLA, M. C. PANGBORN, and R. J. ANDERSON (J. Amer. Chem. Soc., 1936, 58, 636—642).—Cultures of four recently isolated strains (A10, A12, A13, A14) and a new batch of H37 (cf. A., 1927, 1114), grown under identical conditions, are extracted with EtOH and Et_2O; the extracted material is then separated into Et_2O-sol. [further separated into $COMe_2$-sol. fat (I) and -insol. phosphatide (II)] and H_2O-sol. fractions [containing the polysaccharide previously described (*loc. cit.*)]. Further extraction with $CHCl_3$ followed by EtOH–Et_2O removes wax (that from H37 contains little or no sterol). Combined lipins are then isolated from the bacterial residue with EtOH–Et_2O containing 1% HCl; these are sterol-free. The amounts of the various fractions obtained vary considerably. All the (II) isolated have low N contents and generally resemble that previously described (*loc. cit.*). The consts. of the (I) show considerable variation and indicate the presence of 26—32% of free fatty acids. The (I) from A12 and H37 contain small amounts of phthiocol (III); hydrolysis gives (III), trehalose (but no glycerol), anisic, stearic, tuberculostearic, and phthioic acids, and an optically active OH-acid of high mol. wt. The (I) contain 2·47—17·7% of unsaponifiable matter; that from A12 appears to contain a little sterol.
H. B.

Influence of temperature on nitrogen fixation by *Azotobacter*.—See B., 1936, 562.

Nodule bacteria. V. Influence of plant extract as accessory substance on the growth of the bacteria. A. ITANO and A. MATSUURA (Ber. Ohara Inst. landw. Forsch., 1936, 7, 185—214; cf. A., 1935, 530).—Growth of the organisms was accelerated by extracts of seedlings and of germinated and ungerminated seeds in the (descending) order named. Optimum concns. differed with the species of plants examined, being greater for nodule-bearing than for non-nodule-bearing legumes, with non-legumes exhibiting an intermediate effect. The action of the extracts is ascribed to the presence in them of growth-accessory substances rather than to their N or inorg. matter contents.
A. G. P.

Hypothesis concerning bacteriophagy. J. C. WILLIAMS (J. Physical Chem., 1936, 40, 477—479).—The theory is advanced that phage is a suspension of extremely small crystals of one or more of the compounds in the homologous bacteria. Bacteriophagy is thus the seeding of these amorphous compounds by phage particles and their subsequent crystallisation.
M. H. B.

Cultivation of poliomyelitis virus. F. EMERSON (Science, 1936, 83, 324—325).—A discussion.
L. S. T.

Bactericidal effects of vapours from crushed garlic. L. WALTON, M. HERBOLD, and C. C. LINDEGREN (Food Res., 1936, 1, 163—169).—The bacteria were grown on agar subjected for various periods to the vapour. Growth of *B. subtilis* (spores) was inhibited after 4 hr. treatment, that of *Serratia marcescens* after 2 hr., and that of *Mycobacterium butyricum* and *M. smegmatis* after 32 min. Boiled and autoclaved garlic were ineffective.
E. C. S.

Comparison of resistance of bacteria and embryonic tissue to germicidal substances. V. Iodine. A. J. SALLE and A. S. LAZARUS (Proc.

Soc. Exp. Biol. Med., 1935, **32**, 1481—1483).—I has the min. toxicity index and max. PhOH coeff. of all the germicides studied (cf. A., 1935, 1421).
R. N. C.

Bactericidal action of mercury on *B. coli* in continuously flowing water. M. Lisbonne and R. Seigneurin (Compt. rend. Soc. Biol., 1936, **122**, 18—20). R. N. C.

Is the pressor effect of a glycerol extract of adrenal glands due to adrenaline ? R. G. Hoskins and J. S. Gottlieb (Endocrinol., 1936, **20**, 188—191).—The amount of adrenal medullary material extracted has no effect on the pressor effect of the extract, which suggests that the agent responsible is not adrenaline. It is considered to be different from cortin. R. N. C.

Local adrenaline effect after sympathectomy. I. Peripheral vessels. A. M. Wright, J. H. Mulholland, K. L. McCloskey, and F. W. Cotui (J. Lab. Clin. Med., 1935, 20, 947—949).
Ch. Abs. (*p*)

Vagotonin and adrenalinæmia. D. Santenoise, L. Merklen, C. Franck, and M. Vidacovitch (Compt. rend. Soc. Biol., 1936, **121**, 1567—1569).—Vagotonin increases adrenaline secretion. R. N. C.

Effect of various cortico-adrenal extracts on diphtheria toxin *in vivo* and *in vitro*. R. L. Zwemer and C. W. Jungeblut (Proc. Soc. Exp. Biol. Med., 1935, 32, 1583—1588). R. N. C.

Effect of cortico-adrenal extract on the course of bacterial intoxications in guinea-pigs. R. W. Whitehead and C. A. Fox (Endocrinol., 1936, 20, 93—99). R. N. C.

Effects of cattle anterior pituitary extracts and potassium iodide on liver-glycogen in guinea-pigs. R. Holden and E. W. Thurston (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1417—1419).—The depression of liver-glycogen (I) by intraperitoneal injections of anterior pituitary extracts is not modified by previous or simultaneous oral administration of KI. KI alone reduces (I) moderately. R. N. C.

Effects of human anterior pituitary gland on sex organs and thyroid gland of the guinea-pig. P. Kunkel and L. Loeb (Proc. Soc. Exp. Biol. Med., 1935, 32, 1413—1417). R. N. C.

Effect of various anterior pituitary gland preparations on thyroidectomised guinea-pigs. K. C. Morrin and L. Loeb (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1425—1427). R. N. C.

Effect of an alkaline extract of the anterior pituitary on the weight of the spleen and adrenal glands and on the blood-calcium level. H. B. Friedgood (Endocrinol., 1936, **20**, 159—169).—The spleen and cortex are increased in wt. and blood-Ca rises. R. N. C.

Calorigenic action of extracts of the anterior lobe of the pituitary in man. W. O. Thompson, S. G. Taylor, 3rd., P. K. Thompson, S. B. Nadler, and L. F. N. Dickie (Endocrinol., 1936, **20**, 55—63).—Thyrotropic hormone increases basal metabolism in every group of patients where the thyroid tissue can still function. Thyroxine and desiccated thyroid produce calorigenic effects in patients who have become refractory to pituitary extracts. R. N. C.

Action of anterior pituitary hormones on basal metabolism of normal and hypophysectomised pigeons and a paradoxical effect of temperature. O. Riddle, G. C. Smith, R. W. Bates, C. S. Moran, and E. L. Lahr (Endocrinol., 1936, **20**, 1—16).—Prolactin (I), like thyrotropic hormone (II), exhibits calorigenic action, but does not act through the thyroid. Follicle-stimulating hormones and prolan are without effect, as are also luteinising and adrenotropic hormones when free from (I) and (II). (I) and (II) injected simultaneously act synergistically to one another on O_2 consumption. "Growth-hormone" preps. usually contain (I) and (II). The calorigenic effect is reduced by decreasing the temp. from 32° to 20°. R. N. C.

Effect of injections of antuitrin-*S* on the sexually inactive male ground squirrel. B. L. Baker and G. E. Johnson (Endocrinol., 1936, **20**, 219—223). R. N. C.

Substances affecting the ovary from the anterior pituitary and from pregnancy urine. H. W. Niemeier (Klin. Woch., 1935, **14**, 576).—A follicle-stimulating but non-luteinising substance (I) is obtained from the urine of cancer. Another principle that is inactive *per se* but causes luteinisation when combined with (I) is obtained from pregnancy urine or the anterior pituitary. R. N. C.

Relation of potency of anterior pituitary-like hormone to hydrogen-ion concentration. C. A. Elden and M. D. Fellows (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1597—1599).—Potency is max. at p_H 6·1—7·3 ; it is scarcely affected by acid, but varies with the alkali content, being greatly reduced by addition of NaOH, but less changed by an alkaline p_H which develops on storage for 3 months in the cold. The hormone may be protein-like in nature, or carried down with foreign protein at the iso-electric point, p_H 6·1. R. N. C.

(A) **Habituation to the anterior pituitary hormone.** (B) **Production of antihormone in serum of resistant animals.** E. Guyénot, E. Held, and A. Moszkowska (Arch. Sci. phys. nat., 1936, [v], **18**, Suppl., 10—12, 12—14).—(A) When guinea-pigs are treated for 30—40 days with anterior pituitary extracts, they become resistant to the action of the hormones which affect the thyroid and the adrenal cortex and to the crinogenic action (which results in the inhibition of œstrus). The auxogenic action on the development of the ovarian follicle and probably the luteinising action does not show this phenomenon of habituation.

(B) The action of anterior pituitary hormone on the thyroid, adrenal cortex, and the crinogenic action on the ovary of the guinea-pig is inhibited by the serum of another guinea-pig made resistant by prolonged treatment with the hormone, the action on the ovary being less complete than that on the other organs. Antibodies are probably formed in the blood of the resistant animals. No evidence could be obtained of the formation of antibodies against the luteinising or auxogenic actions of the hormone. W. O. K.

Chemical changes in the muscle of the hypophysectomised toad. A. D. Marenzi (Endocrinol., 1936, **20**, 184—187).—Asthenia following removal of the whole pituitary or anterior lobe is accompanied by fall of glycogen, inorg. P, phosphocreatine, and glutathione in skeletal muscle, and by reduced production of lactic acid during tetanic stimulation. Grafts or extracts of the glandular or intermedio-neural lobe of the pituitary relieve asthenia, and cause increases of the above constituents that do not usually reach normal. R. N. C.

Oxytocic hormone of posterior lobe of pituitary gland. J. M. Gulland and S. S. Randall (Chem. and Ind., 1936, 442—443).—The evidence adduced by Sealock and du Vigneaud (A., 1935, 1275) that the oxytocic principle contains a reducible ·S·S· is not conclusive because the agent employed, cysteine, is not sp. for ·S·S·. It is possible that the redox system with E_0' $-0{\cdot}190$ volt at $p_{\rm H}$ 6·0 is actually a ·S·S· $\rightleftharpoons$ ·SH system and that the second redox system with E_0' $-0{\cdot}025$ volt at $p_{\rm H}$ 6·0 is due to a group of as yet unknown nature (cf. Gulland and Randall, *ibid.*, 542). W. O. K.

Depressor substances in the posterior lobe of the pituitary. E. Larson (J. Pharm. Exp. Ther., 1936, **56**, 396—416).—Histamine (I) was present in aq. extracts of the COMe$_2$-sol. and -insol. material of the posterior lobe; EtOH extracts of the latter contained (I) whilst aq. extracts with EtOH gave a ppt. which exhibited oxytocic but not depressor activity. H. D.

Antagonism between posterior lobe pituitary hormones and insulin. H. C. Ellsworth (J. Pharm. Exp. Ther., 1936, **56**, 417—420).—Small doses of the oxytocic hormone depress, and large doses completely inhibit, insulin hypoglycæmia in dogs; the pressor fraction has little or no effect. H. D.

Absence of follicle-stimulating hormone in pituitaries of young pigeons. O. Riddle and J. P. Schooley (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1610—1614).—The hormone appears 1·8 months after hatching in pigeons and 2·5 months after in ring-doves. R. N. C.

Uterine response to pitocin. M. R. White and J. P. Pratt (Endocrinol., 1936, **20**, 17—23). R. N. C.

Reaction of fish to sex hormones. S. E. Owen (Endocrinol., 1936, **20**, 214—218). R. N. C.

Relation of sex hormones to calcium metabolism in the bone marrow. O. Arnold, F. Holtz, and H. Marx (Naturwiss., 1936, **24**, 314—317).—The hypocalcæmia and tetany, which accompanies parathyroid deficiency, may be counteracted by administration of the ergosterol derivative contained in the prep. "A.T. 10." During pregnancy and lactation the quantity of "A.T. 10" required increases several-fold, due, probably, to the presence in the body of increased amounts of sex hormone. W. O. K.

Effect of endocrine gland preparations on allergic reactions (anterior pituitary extract, pregnancy urine extract, follicular hormone). B. Solomonica and R. Kurzrok (Endocrinol., 1936, **20**, 171—173). R. N. C.

Pathological conditions induced by œstrogenic compounds in the coagulating gland and prostate of the mouse. H. Burrows (Amer. J. Cancer, 1935, **23**, 490—512).—Application of ketohydroxy- and trihydroxy-œstrin to the skin of the interscapular region caused lesions in the coagulating gland and the prostate in mice. Ch. Abs. (*p*)

Effects of œstrin injections on accessory reproductive organs of the male ground squirrel (*Citellus tridecemlineatus*). L. J. Wells (Anat. Rec., 1936, **64**, 475—497). R. N. C.

Effect of œstrin on the pituitary gland. W. Cramer and E. S. Horning (Lancet, 1936, **230**, 1056—1057; cf. this vol., 504). L. S. T.

Lack of effect of theelin on somatogenic, thyrotropic, and adrenotropic activity of pituitary. H. B. Shumacker, jun., and A. Lamont (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1568—1570). R. N. C.

Induction of an acid vaginal secretion in the immature macaque by injections of œstrin. B. V. Hall and R. M. Lewis (Endocrinol., 1936, **20**, 210—213).—The $p_{\rm H}$ of the fluid is depressed at least 2 units. R. N. C.

Folliculin and carbohydrate metabolism. J. A. Collazo and F. B. Marti (Ann. Méd., 1935, **38**, 383—388).—Injection of pure folliculin into bitches caused a 30% increase in blood-sugar and a 96% increase in lactic acid. Nutr. Abs. (*m*)

Paradoxical action of folliculin (menformone) in male animals; effect of male hormone. S. E. de Jongh (Arch. int. Physiol., 1935, **50**, 348—378; Chem Zentr., 1935, ii, 1569). R. N. C.

Preparation of the gonadotropic hormone of pregnant mare's blood. E. L. Gustus, R. K. Meyer, and O. R. Woods (J. Biol. Chem., 1936, **114**, 59—63).—The hormone has been obtained from citrated plasma by selective adsorption on Al(OH)$_3$, elution at $p_{\rm H}$ 3·5, and filtration through a Pasteur-Chamberland filter at $p_{\rm H}$ 8·3. H. G. R.

Two gonadotropic substances in mare serum. F. J. Saunders and H. H. Cole (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1476—1478).—The serum contains a stable luteiniser and a gonadotropic hormone which is destroyed by treatment with H$_2$S and incubation, and has not been identified as the follicle-stimulating hormone of Fevold and Hisaw. R. N. C.

Effect of œstrogenic hormones on lactation in the cow. S. J. Folley (Nature, 1936, **137**, 741—742).—Administration of œstrogenic hormone to a lactating cow produces a marked diminution in the daily milk yield, but increases the non-fatty solids content and the milk-phosphatase concn. Secretion of milk-fat is a process not closely related to that of other milk-solids. L. S. T.

Excretion of ovarian hormone by sows during pregnancy. M. Struck (Deut. tierärztl. Woch., 1935, 43, 260—263; Chem. Zentr., 1935, ii, 1568).—Ovarian hormone excretion in the urine occurs in the 3rd and 4th week, ceases at the 5th, and reappears in the 11th or 12th, thence increasing until parturition, after which it disappears for 14 days. R. N. C.

Extraction of both œstrin and gonadotropic hormones from a single blood sample. S. C. Freed (Endocrinol., 1936, 20, 224—225).—Citrated blood is poured into 5 vols. of $COMe_2$, and the ppt. is removed by centrifuging and washed with $COMe_2$. The combined filtrate and washings are evaporated, the residue is extracted with Et_2O, and the Et_2O evaporated off after addition of oil as solvent; the solution contains œstrin. Gonadotropic hormones (I) are extracted from the $COMe_2$ ppt. with 50% EtOH at p_H 4·4, pptd. with 95% EtOH, and extracted twice with a buffer solution at p_H 4·4, which is pptd. twice with 95% EtOH, (I) being removed by centrifuging. R. N. C.

Specificity of the oviduct test for follicular hormone. W. Fleischmann and S. Kann (Klin. Woch., 1935, 14, 644).—The positive reaction given by male hormone (I) preps. such as Testosan is due to their contents of female hormone; cryst. (I) is inactive. R. N. C.

Problem of standardisation of follicular hormone and its derivatives. W. Schoeller, M. Dohrn, and W. Hohlweg (Klin. Woch., 1935, **14**, 826—827). R. N. C.

Excretion of prolan in essential hypertension. M. Scarf and S. L. Israel (Endocrinol., 1936, 20, 180—183). R. N. C.

Gonadotropic substance from teratoma of the testis. S. C. Freed and A. Coppock (Proc. Soc. Exp. Biol. Med., 1935, 32, 1589—1591). R. N. C.

Testicular hormone and Sebright plumage. C. H. Danforth (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1474—1476). R. N. C.

Synthesis of Δ^4-dehydroandrosterone.—See this vol., 854.

Purification of galactin, the lactogenic hormone. W. H. McShan and C. W. Turner (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1655—1656).—The isoelectric ppt. at p_H 5·5—6·5 from the alkaline digest, after dehydration with $COMe_2$ and drying, is extracted repeatedly with AcOH and the extract poured into Et_2O, the ppt. being washed with $COMe_2$ and dried. The ppt. gives the biuret reaction and is active in pigeons in doses of 3 mg. daily. R. N. C.

Insulin and blood-lactic acid. J. A. Collazo and J. Almela (Ann. Méd., 1935, 38, 371—382).—The rise in blood-lactic acid (I) in the dog after lactate ingestion was increased by simultaneous insulin (II) injection. (II) injection alone produced a rise in (I) > that after lactate ingestion alone. This (II) effect is attributed to a compensatory secretion of adrenaline. Nutr. Abs. (*m*)

Rôle of insulin in metabolism in non-diabetic patients. I. Transitory hyperglycæmia and glycosuria following discontinuation of insulin. B. B. Clark, R. B. Gibson, and W. D. Paul (J. Lab. Clin. Med., 1935, 20, 1008—1016).—Effects are ascribed to the action of administered insulin in causing a compensatory inhibition of the normal islet secretion. Ch. Abs. (*p*)

Continuous intravenous injection of insulin in man: limiting dose. A. Baudouin and J. Lewin (Compt. rend. Soc. Biol., 1936, **121**, 1594—1596).—The limiting hypoglycæmic dose in man is 0·01—0·02 international unit per kg. per hr. R. N. C.

Preparation of crystalline insulin free from vagotonin. D. Santenoise, T. Brieu, G. Fuchs, and E. Stankoff (Compt. rend. Soc. Biol., 1936, **121**, 1565—1567).—Commercial insulin (I) is dissolved in HCl at p_H 3, impurities are removed by centrifuging, and (I) and vagotonin (II) are pptd. with LiCl and dried. (I) is then repeatedly pptd. isoelectrically at p_H 5·2. (II) is finally destroyed by incubation for 12 hr. in HCl solution at p_H 1 and 55°, after which p_H is restored to 5·2 with LiOH; after another pptn. at p_H 5·2 (I) is dehydrated and crystallised by Scott's method. R. N. C.

Electrometric titration of insulin. Iodinated insulin. C. R. Harington and A. Neuberger (Biochem. J., 1936, **30**, 809—820).—Titrations of cryst. insulin in aq. and 80% EtOH solution indicate acid- and base-binding capacities of respectively 43 ± 2 and 60—70 groups per mol. (cf. Harvey *et al.*, A., 1934, 602). Iodination gives a product [15·4% I, corresponding with 24 tyrosine (I) groups] in which the (I) groups only are substituted (probably in the 3 : 5 position) and exhibiting 5—10% of the initial hypoglycæmic action (mice, rabbits); partial removal of I by hydrogenation (Pd–$BaSO_4$ in 50% aq. C_5H_5N) produces reactivation approx. $\propto$ the amount of I removed. F. O. H.

Action of various reagents on insulin. H. Jensen, E. A. Evans, jun., W. D. Pennington, and E. D. Schock (J. Biol. Chem., 1936, **114**, 199—208).—Treatment with $0{\cdot}033N$-NaOH, aldehydes, HNO_2, Ac_2O, acid–EtOH, CH_2N_2, MeI, or I caused partial or complete inactivation of insulin (I) and a change in either cystine (II) or NH_2-N content, with the exception of acid–EtOH which had no effect on (II). The physiological activity of (I) cannot be attributed to a localised portion of the mol., but the hypoglycæmic property may be associated with certain ·S·S· groups, and also with certain NH_2 groups, both being present probably as (II). J. N. A.

Mechanism of the action of parathormone on urinary elimination of phosphorus. L. Brull (Compt. rend. Soc. Biol., 1936, **122**, 76—77).—Parathormone (I) increases P excretion in the urine of the dog without affecting plasma-PO_4'''. Isolated normal kidneys perfused with the blood of a (I)-injected dog also excrete more P, but if this is interrupted for 3 hr. with perfusion from a control animal, the isolated kidneys do not re-establish the high P excretion if perfusion from the injected animal is resumed, although the latter's kidneys still show a high P excretion, being no doubt saturated with (I). R. N. C.

Influence of parathormone on the magnesium, calcium, and phosphorus content of human blood. G. Melli and N. Koradimova (Policlinico, 1935, 42, 629—636).—The average effects of 200 units of parathormone on the blood constituents of 10 patients were: Ca rose after 4 hr. to a max. of 13·4 mg. per 100 ml. at the 9th and returned to normal at the 15th hr.; Mg rose from the 1st hr. to a max. of 4·8 mg. at the 3rd and fell to normal at the 4th hr.; P remained practically const. Nutr. Abs. (*m*)

Influence of infection on action of parathyroid hormone in man. G. C. Linder (Quart. J. Med., 1935, 4, 131—137).—Serum-Ca was low and the response to injection of parathyroid hormone small during typhoid fever but increased on recovery. In pulmonary tuberculosis serum-Ca was normal and response to the hormone was greater in active than in quiescent phases, but increased when basal metabolism was raised by thyroid extract. Ch. Abs. (*p*)

Effect of thyroxine on glycolysis of muscular tissue. P. E. Grégoire (Compt. rend. Soc. Biol., 1936, **122**, 103—105).—Thyroxine (I) depresses glycolysis by tissues in presence of glucose alone, but if glycogen (II) is added, glycolysis increases to vals. of the same order as the increased vals. due to addition of (II) to normal tissue without (I). The max. limit of carbohydrate concn. for glycolysis to occur is raised to infinity by (I). R. N. C.

Site and manner of action of thyroxine in the organism. G. Mansfeld (Orvosi Hetilap, 1935, 79, 491—497).—Thyroxine migrates through the nerves into muscular cells and increases their O_2 consumption. Ch. Abs. (*p*)

Action of the thyroid on blood formation. J. von Boros and G. Czoniczer (Klin. Woch., 1935, **14**, 573—575). R. N. C.

Metabolism of isolated surviving tissues from animals rendered hyperthyroid with thyroxine. D. McEachern (Bull. Johns Hopkins Hosp., 1935, 56, 145—179).—Tissue from hyperthyroid animals showed increased O_2 consumption but $<$ that anticipated from the total consumption of the animal. Increased tissue glycolysis was not the cause of the increased O_2 consumption. CN', F', and $CH_2I\cdot CO_2'$ reduced the respiration of hyperthyroid tissue without affecting the mechanism which necessitates an increased O_2 supply. I had no effect. In hyperthyroid animals hepatic and renal tissues retained their ability to oxidise lactate, pyruvate, and succinate. The oxidising capacity of muscle was $>$ normal. Ch. Abs. (*p*)

Thyroglobulin. II. The Van Slyke nitrogen distribution and tyrosine and tryptophan analyses for normal and goitrous human thyroglobulin. J. W. Cavett (J. Biol. Chem., 1936, **114**, 65—73).—The NH_2-acid content of thyroglobulin with the exception of thyroxine (I), di-iodotyrosine (II), and tyrosine (III) is the same in all cases. (III) in the mol. is capable of conversion into (I) or (II), being observed during I medication in pathological cases. H. G. R.

Analyses of thyroglobulin. A. White (Proc. Soc. Exp. Biol. Med., 1935, 32, 1558—1560).—Vals. are given. R. N. C.

Non-thyroid substances with thyroid action. IV. Thyroid-like substances from artificially iodinated protein. J. Abelin (Arch. exp. Path. Pharm., 1936, **181**, 250—258; cf. A., 1934, 814, 1409).—Iodinated proteins, like active thyroid gland substance, are separable into $\not<$ two fractions. Removal of inactive material is achieved by hydrolysis with alkalis (but not with enzymes or acids), especially with 40% $Ba(OH)_2$. Thus iodinated caseinogen (5·17% I) yields preps. (42·2% I), 2×10^{-5} g. of which has an action on the metabolism and resistance to MeCN poisoning of mice characteristic of thyroid preps. F. O. H.

Reid Hunt reaction and the thyrotropic hormone. H. Wiesbader (Endrocrinol., 1936, 20, 100—102).—The resistance of mice to MeCN is not increased by normal serum, but it is increased by pregnancy serum, follutein from pregnancy urine, and thyrotropic hormone. R. N. C.

Anti-thyrotropic activity. I. W. Rowlands and A. S. Parkes (Proc. Roy. Soc., 1936, **120**, **B**, 114—125).—Normal serum of goat, horse, sheep, cow, or rabbit does not show any anti-thyrotropic activity. This may be induced in rabbits in 4 weeks by daily injection of thyrotropic extract and rises to a max. in 10 weeks. H. G. R.

Vitamin deficiency, passage of infection, and resistance to disease. L. Oelrichs (Z. Hyg., 1935, **117**, 684—710). R. N. C.

Experimental calcification in avitaminosis-*A*. A. Escudero and P. Bosq (Semana méd., 1935, 42, 1283—1286; Chem. Zentr., 1935, ii, 1572).—Microscopic intraparenchymatous calcification of the kidneys occurs in avitaminosis-*A* in the rat. R. N. C.

Effect of vitamin-*A* deficiency on development of the retina and on the first appearance of visual purple. K. Tansley (Biochem. J., 1936, 30, 839—844).—Only a moderate deficiency of vitamin-*A* could be developed in young rats during the suckling period. The development of visual purple was retarded and in some cases prevented, whilst the effect on the structure and development of the rods was not so marked. The part played by -*A* in the visual purple system is discussed. J. N. A.

Vitamin-*A* metabolism and liver in experimental phosphorus poisoning. F. Lasch (Klin. Woch., 1935, **14**, 1070—1073).—Vitamin-*A* (I) in the liver of rats and guinea-pigs is unaffected by fatal P poisoning. Parenteral administration of (I) to guinea-pigs simultaneously with poisoning by P results in quant. storage of (I) in the injured liver as in normal animals. R. N. C.

Carotene and vitamin-*A* contents of human serum. E. Schneider and E. Widmann (Klin. Woch., 1935, **14**, 670—673).—Carotene (I) and vitamin-*A* (II) can be demonstrated in serum, but not in corpuscles. A life-curve of serum-(II) can be defined, from which the presence of hypovitaminosis can be determined; such hypovitaminosis when the diet is complete is due to liver injury. (I) and (II), but not ascorbic acid, increase glycolysis. R. N. C.

Vitamin-*A* content of West Indian shark (*Carcharinus* sp.) liver oil. C. F. Asenjo, L. M. Dalmau, and J. H. Axtmayer (Puerto Rico J. Publ. Health, 1935, **11**, 158—162).—The vitamin-*A* val. of the oil from sharks caught during July was about 13,300 Sherman units per g. Nutr. Abs. (*m*)

Determination of vitamin-*A* by means of its influence on the vaginal contents of the rat. W. Hohlweg and M. Dohrn (Biochem. J., 1936, **30**, 932).—Claim of priority as to this method over Coward *et al.* (this vol., 253). P. W. C.

Determination of vitamin-*A*. G. Balassa and G. Szántó (Z. physiol. Chem., 1936, **240**, 29—32).—Addition of guaiacol may be omitted from Rosenthal's test for vitamin-*A* (A., 1934, 225, 1145), 0·2% aq. para-brown Z extra being a suitable comparison standard. Cholesterol and tissue extracts give unstable red solutions with the $SbCl_3$ reagent. Photometric data of light absorption by the reacted solution are discussed. F. O. H.

Correlation of vitamin-*A* and -*B* with the calcinosis factor. F. Widenbauer (Klin. Woch., 1935, **14**, 901).—Calcinosis poisoning in mice by vigantol or "A.T. 10" is checked by simultaneous large doses of vitamin-*A* and -*B*. R. N. C.

Avitaminosis-*B* and muscular glycolysis. P. E. Grégoire (Compt. rend. Soc. Biol., 1936, **122**, 101—103).—Total inorg. and hydrolysable PO_4''' in the rat are both depressed in avitaminosis-*B*. Mg is increased in avitaminosis-*B* but not in starvation. R. N. C.

Variations of the respiratory quotient and basal metabolism during avitaminosis-*B*. J. M. Joly (Compt. rend. Soc. Biol., 1936, **122**, 196—199).—The R.Q. in pigeons is lowered, but basal metabolism is increased. R. N. C.

Production of avian polyneuritis by the addition of lactic acid to diets rich in sugar, protein, or fat, containing considerable quantities of the *B* vitamins. R. Lecoq (Compt. rend., 1936, **202**, 1304—1307).—Even with an excess of vitamin-*B*, development of polyneuritis is caused by accumulation of lactic acid in the tissues, when 10% is present in the diet. H. G. R.

Requirements of the flour-beetle (*Tribolium confusum*, Duval) for vitamins in the *B* group. H. R. Street and L. S. Palmer (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1500—1501).—The larvæ require vitamin-B_1 and also a thermostable factor which is destroyed by autoclaving at p_H 13. R. N. C.

***B*-Vitamins in human urine.** M. H. Roscoe (Biochem. J., 1936, **30**, 1053—1063).—Vitamin-B_1 and -B_2 were determined in the urine of 3 controls and one case of "alcoholic" polyneuritis. All cases received a known diet for 12 days, and then the same diet+a known daily amount of *B*-vitamins for 12 days. The conc. urine was fed to rats deprived of -B_1 and -B_2, respectively. -B_1 was determined by the power to cure neuritis and -B_2 by promoting growth. -B_1 was not present in the urine of the controls in the first period, but addition of 720 international units daily caused a daily excretion of 167—333 units. -B_2 was present in small amounts, and feeding of -B_2 increased the amount excreted. In the case of "alcoholic polyneuritis," the initial excretions of -B_1 and -B_2 were comparable with those of the controls. With added -B_1 and -B_2 the retentions were respectively slightly < and slightly > those of the controls. J. N. A.

Effect of some reagents on the "filtrate factor" (water-soluble vitamin belonging to the vitamin-*B* complex and preventing a dietary dermatitis in chicks). S. Lepkovsky and T. H. Jukes (J. Biol. Chem., 1936, **114**, 109—116).—The factor can be conc. from aq. rice bran extract by pptn. of inert matter with fuller's earth and MeOH. It is slightly inactivated by warming with NaOH and completely with NaOH and $FeCl_3$ and is not appreciably adsorbed from acid solution or pptd. by $Pb(OAc)_2$. H. G. R.

Distribution of the "filtrate factor" (water-soluble vitamin belonging to the vitamin-*B* complex and preventing a dietary dermatitis in chicks) in certain feeding stuffs. T. H. Jukes and S. Lepkovsky (J. Biol. Chem., 1936, **114**, 117—121).—On suboptimal levels the growth of the chicks approx. ∝ the quantity of the factor fed. The relative vals. of common feeding stuffs are given. H. G. R.

Biochemical lesion in vitamin-B_1 deficiency. Application of modern biochemical analysis in its diagnosis. R. A. Peters (Lancet, 1936, **230**, 1161—1165).—A lecture. L. S. T.

Vitamins in human nutrition. Excretion of vitamin-B_1 in human urine and its dependence on the dietary intake. L. J. Harris and P. C. Leong (Lancet, 1936, **230**, 886—894).—The daily excretion of vitamin-B_1 in human urine has been measured by the Harris bradycardia method. Healthy adults on normal diets excrete 12—35 international units with an average of 20 per day (approx. 5—8% of the daily intake). The proportion of -B_1 excreted is markedly < that of -*C* under comparable conditions. With a diet containing comparatively large or small amounts of -B_1 the amounts excreted increase or decrease proportionally. In hypovitaminosis-B_1 in rats the amount excreted is negligible. In avitaminosis (beri-beri) in man excretion of -B_1 may almost cease. A daily intake of 200 units for a man of 10 stone wt. may be fixed as a provisional min. allowance and an excretion of < 12 units indicates a diet containing < the normal allowance of -B_1. -B_1 is absorbed from urine by shaking with acid clay and if dried, the activated clay retains its full activity after 3 months' storage in a refrigerator. L. S. T.

Adsorption and elution of vitamin-B_1. W. H. Schopfer (Arch. Sci. phys. nat., 1936, [v], **18**, Suppl., 6—10).—Vitamin-B_1, adsorbed on fuller's earth as in the international standard powder, is eluted but slightly when treated at 115° for 15 min. with buffer solution of low p_H, but is extracted at higher p_H with a max. at p_H 6—7. When the powder is added to a culture of *Phycomyces* growth is stimulated apparently as a result of the elution and utilisation of the vitamin in the cold. W. O. K.

Measurement of vitamin-B_1 activity by means of a micro-organism (*Phycomyces*). W. H. Schopfer and A. Jung (Arch. Sci. phys. nat., 1936, [v], 18, Suppl., 22—25).—Assay of vitamin-B_1 preps. by means of their action on the growth of *Phycomyces* yields results in general agreement with those obtained by the usual rat method. Divergences sometimes occur, more especially in the case of crude preps. W. O. K.

Crystalline torulin (as vitamin-B_1) and the international vitamin-B_1 standard. H. W. Kinnersley and R. A. Peters (Biochem. J., 1936, 30, 985—991).—1 International unit of vitamin-B_1 is approx. equiv. to 2×10^{-6} g. of cryst. -B_1 hydrochloride, the val. being the same whether given orally or by injection. The day dose method for pigeons by injection may be used for impure but not for cryst. specimens. H. G. R.

Vitamin-B_1 and -B_2 content of Arizona-grown grapefruit and broccoli. G. H. Roehm (J. Home Econ., 1935, 27, 663—666).—Grapefruit peel and pulp contained $\ngtr$ 0·28 Sherman units of -B_1, but the fresh peel contained 1·0 unit of -B_2 and the boiled peel 0·5 unit. Broccoli leaf and flowers contained 4·0 and 3·0 units, respectively, of -B_2 and 0·66 and 0·5 unit, respectively, of -B_1. Nutr. Abs. (*m*)

Water-soluble *B*-vitamins. V. Two types of skin lesion occurring in vitamin-B_2 deficiency in the rat in relation to deficiency of flavin and vitamin-B_6, respectively. VI. Flavin and vitamin-B_6 in cereals. A. M. Copping (Biochem. J., 1936, 30, 845—848, 849—856; cf. A., 1935, 544).—V. With young rats maintained on diets lacking only one constituent of vitamin-B_2, those deprived of flavin (I) developed the (*b*) type of skin lesions, whilst those deprived of -B_6 developed the florid (*a*) type of dermatitis. Cures were effected in the first case by feeding pure (I), and in the second by administration of -B_6 as an EtOH extract of whole maize or wheat.

VI. Wheat and maize are good sources of vitamin-B_6, 25—33% of which could be extracted by cold 80% EtOH. Wheat contains more (I) than maize, but none is extracted by cold 80% EtOH. The germ and integuments of wheat and maize contain more -B_6 than the endosperm. Maize and its extracts may contain a deleterious substance which is extracted by cold 80% EtOH, and this possibly is related to endemic pellagra. J. N. A.

(A) Vitamin-B_2 complex in distiller's yeast, No. 12. V. V. Efremov and N. Jarussova. **(B) Vitamin-B_2 complex in millet.** V. V. Efremov (Problems of Nutrition, Moscow, 1935, 4, No. 6, 137—139, 139—141).—(A) The yeast contained about 40,000 Sherman units of -B_2 per kg. (B) The amount of -B_2 per kg. in millet was $>$ 300 and $<$ 1000 Sherman units. Nutr. Abs. (*m*)

Vitamin-B_2. W. von Drigalski (Klin. Woch., 1935, 14, 773—775).—Vitamin-B_2 (I) is present in cow's, goat's, and human milk, in " campolon " (II), but not " hepracton " liver extract, and in cerebrospinal fluid; it is frequently demonstrable in blood-serum, in which it is increased by (II) treatment. It is probably not identical with the exogenous factor for pernicious anæmia therapy. Contrary to -*A*, blood-(I) exhibits only small upward fluctuations. R. N. C.

Effect of *Capsicum annuum* on serum-protein. S. Lee (J. Severance Union Med. Coll., 1935, 3, 31—32).—The feeding to rabbits of 1 g. daily of *C. annuum*, which is very rich in vitamin-*C*, reduced the protein content of the serum. Nutr. Abs. (*m*)

Action of ascorbic acid on metabolism and on blood. L. Armentano, A. Bentsáth, A. Hámori, and A. Korányi (Z. ges. exp. Med., 1935, 96, 321—327; Chem. Zentr., 1935, ii, 1573).—Ascorbic acid does not play an essential part in carbohydrate metabolism, and does not affect the composition, catalytic effect, or basal exchange of blood. R. N. C.

Ascorbic acid and blood-catalase. III. Hormonal relations. G. Török, M. Hedry, and R. Neufeld (Klin. Woch., 1935, 14, 673—675).—Ascorbic acid (I) reduces the temporary increase of blood-catalase (II) caused by unilateral adrenalectomy, and increases the fall of (II) caused by thyroidectomy in rabbits. Its effect after removal of the sex glands or spleen is variable. (I) does not increase (II) in animals given vitamin-free diets after removal of any of the above glands. R. N. C.

Ascorbic acid as a precursor of serum complement. E. S. Horgan (Nature, 1936, 137, 872).—The results of Marsh (this vol., 765) are supported. L. S. T.

Effect of incomplete diets on the concentration of ascorbic acid in the organs of rats. S. S. Zilva (Biochem. J., 1936, 30, 857—867; cf. A., 1935, 262).—The total amounts of ascorbic acid (I) in the liver and intestines of rats on a stock diet increased as the rats grew, but the concns. remained approx. the same. In rats starved for 48 hr. the concn. of (I) in the liver was the same, but the intestines showed a rise, due possibly to a loss in wt. of the intestine. A carbohydrate diet had a detrimental effect, but the concn. of (I) in the livers and intestines was similar to those for normal rats. Rats on a protein–fat diet throve worse than on a carbohydrate diet, but there was no increase of (I) in the liver or intestines. The hypothesis of Hopkins and Slater (this vol., 254) is not fully supported by experimental evidence. J. N. A.

Histochemistry. VII. Concentration of vitamin-*C* in the thymus in relation to its histological changes at different stages of development and regression. D. Glick and G. R. Biskind (J. Biol. Chem., 1936, 114, 1—7).—The concns. in the whole gland for the fœtus and calf, steer, and cow and bull are 0·35—0·52, 0·23—0·36, and 0·04—0·17 mg. per g., respectively. These vals. are approx. the same on the fat- and connective tissue-free basis. H. G. R.

Amount of vitamin-*C* required to maintain the normal reducing power of animal tissues. L. De Caro (Z. physiol. Chem., 1936, 240, 179—190).—In guinea-pigs on scorbutic diets, ascorbic acid (I) disappears almost completely from the adrenals in 10—13 days, the curve expressing the rate of disappearance being approx. exponential. The amounts (12 mg. or 10 g. of cabbage) of (I) which must be given daily in order to maintain normal reducing power in the adrenals and liver are much > those required for prevention and cure of scurvy. Naturally-occurring (I) in food is better utilised than isolated (I) and injected (I) than (I) given orally. The preventive and curative effects of daily injections of 12 mg. of "Maurer's acid" (A., 1933, 936) are equiv. to daily injections of 5 mg. of (I). The (I) of tissues not required for prevention of scurvy is less a reserve than a factor for maintaining optimal functioning of the cells. W. McC.

Ascorbic acid content of blood. C. J. Farmer and A. F. Abt (Proc. Soc. Exp. Biol. Med., 1935, **32**, 1625—1629).—To determine ascorbic acid (I) oxalated blood is centrifuged and the plasma deproteinised with H_2WO_4 and titrated with 2 : 6-dichlorophenol-indophenol. Oxidised (I) cannot be determined by reduction with H_2S, as colloidal WS_2 interferes. $CCl_3{\cdot}CO_2H$-deproteinisation gives slightly higher vals. owing to a less definite end-point, but permits the determination of oxidised (I). R. N. C.

Content of vitamin-*C* in normal and pathological [human] cerebrospinal fluid. G. Marinesco, G. Alexianu-Buttu, and I. Olteanu (Bull. Acad. Sci. Roumaine, 1936, **17**, 129—137).—The normal content increases with increasing age; considerable variations occur in pathological conditions. H. G. R.

Vitamin-*C* in saliva. O. H. Stuteville (Proc. Soc. Exp. Biol. Med., 1935, 32, 1454—1455).—The vitamin is present in concn. 0·0025 mg. per c.c. R. N. C.

Ascorbic acid content of the ovary and corpus luteum at different stages of the œstrous cycle. A. A. Policard and M. Ferrand (Compt. rend. Soc. Biol., 1936, **122**, 200—202).—The ascorbic acid content of the corpus luteum at various stages of formation is approx. const. and equals that of the ovary. The content of the residual ovarian tissue is also relatively const. R. N. C.

Fresh vegetables rich in vitamin-*C*.—See B., 1936, 568.

Vitamin-*C* content of apples and its relation to human welfare. W. F. Dove and E. Murphy (Science, 1936, **83**, 325—327).—As with the fruits, the vitamin-*C* content of the leaves of the Northern Spy apple is > that of the McIntosh apple. L. S. T.

Vitamin studies on apples. I. A. Manville, A. S. McMinis, and F. G. Chuinard (Food Res., 1936, **1**, 121—140; cf. A., 1935, 414).—The vitamin-*A* and -*C* contents of Arkansas Black apples were 36 and < 2·5 units per oz.; of Baldwin, 15 and 2·5—3·0; of Jonathan, 24 and 1·5—2·0; of Winesap, 36 and 3·0; of Delicious, 24 and < 2·5; of Gravenstein, 14—17 and 3·75; of Spitzenberg, 36 and 7. The three last-named do not form a good source of -*B*. During storage, -*A* is destroyed < -*C*, the decomp. of the latter varying with the type of apple. Careful removal of the peel does not markedly decrease the -*C* content. A new (biological) method for the determination of -*A* is proposed. E. C. S.

Specific reaction for the detection and determination of ascorbic acid in serum. H. Lund and H. Lieck (Nature, 1936, **137**, 784).—The addition of small amounts of ascorbic acid to a solution of methylene-blue results in complete decolorisation in < 30 sec. on exposure to strong light. This reaction is not produced or inhibited by glutamine, ergothionine, creatine, creatinine, urea, adenine, guanine, hypoxanthine, xanthine, uric acid, cystine, hæmoglobin, and PhOH. L. S. T.

Determination of vitamin-*C* in various foods and in human urine. R. Casazza (Arch. Ist. Biochim. Ital., 1936, 8, 39—62).—Data are given and discussed for the ascorbic acid (I) content (determined iodometrically) of *Citrus* fruits and of human urine following ingestion of (I)-free and -rich meals and intravenous injection of (I). F. O. H.

Influence of milk constituents on the effectiveness of vitamin-*D*. G. C. Supplee, S. Ansbacher, R. C. Bender, and G. E. Flanigan (J. Biol. Chem., 1936, **114**, 95—107).—A "symplex" (A., 1934, 913) of vitamin-*D* and lactalbumin is formed when the latter is pptd. from solution containing the vitamin. The biological activity of the system is > that of its components and is increased still further if lipin-free lactalbumin is used. H. G. R.

Colour reaction for the detection and determination of vitamin-*D*. W. Halden (Naturwiss., 1936, **24**, 296—297; cf. following abstract).—A solution of the prep. (oils are first saponified and extracted) in anhyd. petrol, C_6H_6, or $CHCl_3$ is treated with 1% pyrogallol in abs. EtOH, 10% $AlCl_3$ in abs. EtOH is added to the conc. solution, and the mixture is heated at 100° for 4 min. W. O. K.

Colour reaction for the detection and determination of vitamin-*D*. W. Halden and (Mrs.) H. Tzoni (Nature, 1936, **137**, 909; cf. preceding abstract).—The reaction detects $\nless$ 0·002 mg. of vitamin-*D*. -*A* and related products must be absent, but cholesterol, ergosterol, and lumisterol do not react. Suprasterol II gives a fainter tint. L. S. T.

Vitamin-*E*. III. S. Ueno, Y. Ota, and Z. Ueda (J. Soc. Chem. Ind. Japan, 1936, **39**, 110—112b).—Feeding experiments (albino rats) with a basic sterility diet to which the vitamin-*E* fraction from rice oil (A., 1935, 1037) had been added confirm the anti-sterility action of the latter. J. W. B.

Vitamin-*E* and the gonads. W. Saphir (Endocrinol., 1936, 20, 107—108).—Commercial preps. of wheat-germ oil exhibit no œstrogenic, gonadotropic, or luteinising effects in rats. R. N. C.

Mode of action of vitamin-*K*. H. Dam, F. Schønheyder, and E. Tage-Hansen (Biochem. J., 1936, 30, 1075—1079; cf. this vol., 907).—Prothrombin (I) can be pptd. from the plasma of normal chicks by $COMe_2$ or AcOH, whilst the ppts. from the plasma of *K*-avitaminous chicks are inactive. The ppt. of (I) from normal chicks is still active after removal of lipins by $COMe_2$ and Et_2O, and the lipins so obtained are inactive. A concentrate of -*K* does not accelerate *in vitro* clotting of plasma+thrombokinase. (I) pptd. by AcOH and washed with $COMe_2$ and Et_2O contains -*K*. J. N. A.

Occurrence and chemical nature of vitamin-*K*. H. Dam and F. Schønheyder (Biochem. J., 1936, **30**, 897—901).—The vitamin-*K* (antihæmorrhagic factor) content of numerous substances is determined and green vegetables are shown to be a particularly rich source. Cold saponification of hog-liver fat destroys one third and hot the whole of the -*K* content. The fatty acid fraction is inactive but enhances the activity of the unsaponifiable fraction. -*K* is thermostable. $COMe_2$ is the most efficient solvent for extraction of -*K* from lucerne leaves. Various methods of purification of the extracted material were tried. Al_2O_3 adsorbed -*K* but elution was unsuccessful. Using the $CaCO_3$ and cane sugar methods, concns. of 6×10^5—10^6 units per g. were obtained. P. W. C.

Purification of the antihæmorrhagic vitamin. H. J. Almquist (J. Biol. Chem., 1936, **114**, 241—245; cf. A., 1935, 1401).—The hexane extract of lucerne meal is treated with MgO and C to remove pigments, then conc., fats and sterols are separated by chilling, the filtrate is evaporated to dryness, and the residue extracted with MeOH; further impurities are removed by chilling. A yellow oil, active in a daily dose of 2 mg. per kg. of diet, was separated by dilution with H_2O. The residue from the aq. MeOH solution was inadequate at twice this level. The vitamin is stable to heat and light but is alkali-labile. H. D.

Determination of vitamin-*K*. I. F. Schønheyder (Biochem. J., 1936, **30**, 890—896; cf. Dam, A., 1935, 903).—The delay in clotting is not due to lack of thrombokinase, insufficiency of fibrinogen, or accumulation of anti-coagulants. In diseased chicks serum-Ca is usually low and inorg. P always high. Addition of $Ca^{\cdot\cdot}$ to the plasma of diseased chicks does not shorten the clotting time. The p_H and salt content of the plasma are normal. After addition of thrombokinase, the amount of thrombin produced in diseased is much < in normal plasma. Normal plasma contains excess of material which accelerates clotting in the blood of chicks deficient in -*K*. *K*-Avitaminosis is prevented by giving dried pig's liver as 20% of the diet (10% affords partial protection) and is cured by giving 11·3 mg. of the liver per g. of chick daily for 3 days. Degree of -*K* deficiency is expressed by the ratio of the concns. of coagulant (1 drop to 5 drops of plasma) required to clot diseased and normal plasma in 3 min. at 40°. 1 unit of -*K* is contained in the min. daily dose of substance per g. of chick which reduces the ratio to 1 in 3 days. W. McC.

Photochemical reaction of chlorophyll with ferrous ions. K. Weber (Nature, 1936, **137**, 870).—Critical (cf. this vol., 11). The bleaching action of $FeSO_4$ on chlorophyll (I) in neutral and in H_2SO_4 solution is not affected by irradiation with a strong C arc. The photochemical reaction between (I) and $FeSO_4$ does not occur according to the equation given by Weiss, and it is not analogous to the photochemical reduction of vat dyes. L. S. T.

Number of chlorophyll molecules acting as an absorbing unit in photosynthesis. H. I. Kohn (Nature, 1936, **137**, 706).—Measurements of the O_2 liberated by a thin suspension of *Chlorella pyrenoidosa* in intermittent light from a Ne discharge tube indicate that the absorption unit within the plant is equiv. to approx. 500 chlorophyll mols. per quantum. The unit is not a rigid structure, and quanta absorbed by a no. of units are pooled in order to reduce 1 mol. of CO_2. L. S. T.

Photoperiodism and changes in the enzymic system [of plants]. N. Krassinski, A. A. Kondrashova, and N. I. Vinogradova (Ann. Bot., 1936, **50**, 293—304).—An artificially shortened day period increased the catalase and peroxidase activity of bean leaves and pods and of chrysanthemum leaves, decreased that of amylase (I) and invertase (II) in beans, and decreased (I) and increased (II) in chrysanthemum. No definite changes occurred in cineraria leaves. Relations between these changes and photoperiodic effects are discussed. A. G. P.

Rate of increase of fluorescence of living leaves. H. Kautsky and A. Marx (Naturwiss., 1936, **24**, 317).—The fluorescence in the leaves of *Ageratum mex*, *Parietaria officinale*, and *Piper nigrum* following illumination after being kept in the dark has been accurately measured with a photo-electric cell. The activation of the chlorophyll–O_2 complex by light follows a unimol. course. W. O. K.

Isotopic fractionation of water by physiological processes. M. Dole (Science, 1936, **83**, 351).—A correction applied to Washburn and Smith's data indicates a preferential rejection rather than selection of D (cf. A., 1934, 570). L. S. T.

Absorption and accumulation of solutes by living plant cells. VIII. Effect of oxygen on respiration and salt accumulation. F. C. Steward, W. E. Berry, and T. C. Broyer (Ann. Bot., 1936, **50**, 345—366; cf. A., 1934, 708).—The previously observed influence of $[O_2]$ on the absorption of $K^{\cdot}$ and Br' by potato discs is confirmed in carrot and artichoke. Respiratory changes are affected only when the $[O_2]$ of the air current is < that of the atm. Aërobic but not anaërobic metabolic processes are concerned in salt accumulation. A. G. P.

Vital oxidation of plant cells by complex cobaltammines. A. Watanabe (Iwata Inst. Plant Biochem., Publ. 2, 1936, 88—96).—The oxidation of various natural OH-compounds, such as myricetin, quercetin, etc., in presence of complex Co ammine salts, is accompanied by a rise in p_H due to the liberation of NH_3. The increasing alkalinity causes an autocatalytic increase in reaction velocity. M. S. B.

Transport of nitrogenous substances under the influence of differences of humidity. M. P. Both (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 531—540).—Transport from leaf to leaf through the sieve tubes is established. A. G. P.

Nitrogen metabolism of the pea seedling. P. McKie and J. Barnett (Biochem. J., 1936, **30**, 1010—1013).—During 32 days' growth from seed, insol., protein-, and NH_2-N represent > 95% of the total N in the plant of *P. sativum*. α-NH_2-acids increase from 2% in the seed to 25% on the 18th day. After an initial decrease, protein-N rises to a const.

val. of 40%. In etiolated seedlings, amide is produced at the expense of NH_2-acids. H. D.

Plant nutrition. IV. Nitrogen metabolism in relation to nutrient deficiency and age in leaves of barley. F. J. Richards and W. G. Templeman (Ann. Bot., 1936, **50**, 367—402; cf. A., 1932, 660).—Comparison of the N contents of successively developing leaves of sand-cultured barley indicates that deficiency of N supplies although lowering the general N level of the plants involved no fundamental change in the N cycle. Deficiency of P causes a decline in the protein content of leaves from the early stages of development, marked accumulation of amide-N, and smaller accumulation of NH_2-N and of NO_3' in later leaves. Protein synthesis is probably checked at the stage of asparagine production. Deficiency of K is marked by disappearance of protein from older leaves, increased proportions of amide- and NH_2-N, and, in later leaves, an accumulation of NO_3'. K is not primarily concerned in protein formation, but is essential to the maintenance of the protoplasmic complex, the breakdown of which leads to rapid proteolysis. Relations between the increase in NO_3' following P and K deficiency, the proportion of NH_2-N, and reductase activity in leaves are discussed. A. G. P.

Changes in the nitrogenous fractions in stored apples. J. P. Howarth, W. H. Pearsall, and R. Wright (Proc. Leeds Phil. Soc., 1936, **3**, 249—255).—Structural breakdown in stored apples follows the period when the sol. N content is a min., and hence cannot be related to hydrolysis of protoplasmic protein. Loss of N from the cortex is considerable in the early period of storage. Changes in N fractions are retarded at low temp. A. G. P.

Phosphorus metabolism of acorns during germination in darkness. E. Michel-Durand (Compt. rend., 1936, **202**, 503—505).—At the beginning of germination 2/3 of the total P of the seed is in acid-sol. forms of which a half is inorg. After 80 days 70% of the total P has passed into the seedling. Translocation of all forms of P occurs, but that of phytin (I) is the most complete. (I) and inorg. P are localised chiefly in roots, and lipin-P in the aerial organs. A. G. P.

Fat metabolism in plants, with special reference to sterols. II. Differential changes in the cotyledons, roots, stems, and leaves. P. L. MacLachlan (J. Biol. Chem., 1936, **114**, 185—191; cf. this vol., 532).—During germination of soya beans, the total fat of the cotyledons decreased, the effect being more marked in light than in darkness. The roots, stems, and leaves synthesised fat equally well in the light and dark. The degree of saturation of the fatty acids was the same in cotyledons and seeds, but was greater in the newly formed acids of roots, stems, and leaves. There was an increase of sterol (I) in roots, stems, and leaves, whilst (I) esters were present in the cotyledons. A close relation probably exists between the metabolism of (I) and the utilisation of fat in the cotyledons. (I) is a vital constituent of roots, stems, and leaves. J. N. A.

Metabolism of the colourless alga, *Prototheca zopfii*, Krüger. H. A. Barker (J. Cell. Comp. Physiol., 1935, **7**, 73—93).—The alga cannot develop in absence of complex org. compounds such as are present in yeast autolysate. It can utilise N from both NH_3 and more complex N compounds, the N content of the cells varying from 1 to 10% according to the amount of N available. The alga can utilise fatty acids, hexoses, and some alcohols, but not OH-, keto-, or dibasic acids. Glucose is converted aërobically into cell material and CO_2; anaërobically it is fermented quantitatively to lactic acid. R. N. C.

Vitamins and plants. A. I. Virtanen (Nature, 1936, **137**, 779—780).—Vitamin-*C* is essential to the growth of pea seedlings. By removing the cotyledons at a suitable stage, the seedlings are deprived of 90% of their -*C* and die or remain dwarfed. The addition of -*C* to the cotyledon-less seedlings assists development and the production of normal blossoms. L. S. T.

Formation of vitamin-*C* in germinating seeds. A. I. Virtanen and L. V. Eerola (Suomen Kem., 1936, **9**, B, 13).—Production of vitamin-*C* by germinating seeds is independent of light, but is greater when the temp. of germination is relatively low, and is inversely ∝ the rate of germination. The -*C* content of seedlings is relatively high when the H_2O supply is low, is influenced by the p_H of the seed (optimum 6·3—6·6), and is increased by addition of PO_4''' (but not by that of sugar) to the nutrient medium. A. G. P.

Germination of leguminous seeds and urease activity. B. N. Sastri and B. A. S. Iyengar (Current Sci., 1935, **4**, 407).—The activities of germinated are always > those of the ungerminated seed extracts. In powdered seed materials differences are small. Part of the urease exists in seeds in an unextractable condition (desmo-urease), converted during germination into an extractable lyo-form. H. G. M.

Physiology and chemistry of the plant hormones. K. V. Thimann (Current Sci., 1936, **4**, 716—721).—A review.

Influence of glucose on auxin production by the root-tip of *Vicia faba*. M. H. van Raalte (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 261—265).—Glucose favours the accumulation of auxin and may also induce the formation of additional auxin in the root-tips. A. G. P.

Interaction of factors in growth of *Lemna*. H. L. White (Ann. Bot., 1936, **50**, 403—417; cf. this vol., 532).—The effects of varying levels of N supply on the rates of multiplication and of respiration, on dry matter production, and on the starch, protein, and chlorophyll contents are examined. Accumulation of carbohydrates in N-deficient plants results from retarded multiplication associated with lowered carbohydrate consumption in growth, and is accentuated by decreased respiration leading to a high net assimilation rate. Decreasing N supply is associated with low amylolytic activity. Changes during recovery from N starvation are examined. A. G. P.

Action of alkaline extract of the anterior pituitary on (A) growth of plants, (B) germin-

ation. E. C. D. Pascal (Rev. soc. argentina biol., 1935, 11, 57—67, 68—94).—(A) Small doses of the extract accelerated the growth of some but not all plants examined. Large doses caused root damage and inhibited growth.

(B) Pre-soaking seeds in the extract accelerated germination in some cases. The extract probably contains two active factors. Ch. Abs. (*p*)

Effect of *X*-irradiation on auxins and plant growth. F. Skoog (J. Cell. Comp. Physiol., 1935, 7, 227—270). Auxin (I) in solution is inactivated by moderate irradiation in presence of O_2, which is required for formation of the oxidisers responsible for the inactivation. Inactivation also takes place in white light in presence of eosin. Extracted heteroauxin and indolylacetic acid are also inactivated in aq. solution. Irradiation inactivates the (I) normally present in plants; it inhibits (I) formation in young *Pisum* and *Vicia*, but not in *Avena* coleoptile, and does not affect (I) transport. (I) applied to irradiated plants causes renewed growth. Lateral bud development caused by irradiation is correlated with loss of (I). The inhibition of growth is due largely to interference with (I) formation. R. N. C.

Effects of ethylene on the plant growth hormone. F. F. Nord (Science, 1936, 83, 284).—A discussion. L. S. T.

Effect of ascorbic acid and indolylacetic acid on regeneration of willow branches and germination. W. Davies, G. A. Atkins, and P. C. B. Hudson (Nature, 1936, 137, 618).—Dil. solutions of ascorbic (I), β-indolyl-acetic (II) and -propionic (III) acids stimulate root and shoot regeneration in willow branches, but at concns. of 1 in 2500 regeneration is retarded by (I) and practically prevented by (II) and (III). (II) and (III) apparently retard the germination and growth of oats and mustard and cress seeds, but (I) stimulates in dil. solutions. At higher concns. (1 : 10^3), (I) shows a retarding effect, whilst (II) and (III) are practically lethal. L. S. T.

Stimulation of root-hair growth in legumes by sterile secretions of nodule bacteria. H. G. Thornton and H. Nicol (Nature, 1937, 137, 494—495).—Addition of a sterile filtrate containing secretions of nodule bacteria deforms and increases the no. and length of the root hairs of lucerne seedlings. L. S. T.

Stimulation of development of plants and of ripening of their fruit by ethyl alcohol and by temporary asphyxia of the roots.—See B., 1936, 467.

Factors affecting nodule formation on seedlings of leguminous plants. C. A. Ludwig and F. E. Allison (J. Amer. Soc. Agron., 1935, 27, 895—902).—In sand cultures nodulation of lucerne and soya bean was increased in many cases by the presence of other plants, including maize and wheat. In the absence of older plants additions of sugar and, in some instances, of small amounts of available N were beneficial. Cold-H_2O extracts of sand in which lucerne, maize, or wheat seedlings had been growing did not affect nodulation of lucerne when added to sand cultures. Presence of other plants may produce conditions in the rhizosphere (including liberation of bacterial growth-promoting substance) more favourable to bacterial development. A. G. P.

Growth, chemical composition, and efficiency of normal and mosaic potato plants in the field. W. E. Stone (J. Agric. Res., 1936, 52, 295—309).—Infected plants had lowered % of sugar and starch and an increased % of ash (dry matter basis). C assimilation per unit leaf area was smaller. A. G. P.

Determination of potassium carbonate in sunflower ash. V. K. Zolotuchin (J. Appl. Chem. Russ., 1936, 9, 552—554).—1 g. of ash is extracted with 150—200 ml. of boiling H_2O for 10 min., the cooled solution is diluted to 250 ml., and 50 ml. of the filtered solution are titrated with 0·1*N*-HCl. A deduction of 0·3 ml. of acid per 100 ml. of solution is made, to correct for solubility of $CaCO_3$. R. T.

Comparison between the Benedict–Denis and Parr bomb methods for determining total sulphur in plants and proteins. E. P. Painter and K. W. Franke (J. Biol. Chem., 1936, 114, 235—239).—The Parr bomb method gave higher vals. for total S in cereal and proteins than the Benedict–Denis method (A., 1911, ii, 66); the latter gave particularly low vals. with cystine and methionine. The Na_2O_2 fusion method gave good vals. in all cases. H. D.

Cyanophoric plants of the Maquiling region. V. J. B. Juliano and M. Guerrero (Philippine Agric., 1935, 24, 22—26).—HCN is recorded in a large no. of species. Ch. Abs. (*p*)

Recovery of hydrocyanic acid from fumigated *Citrus* leaves. E. T. Bartholomew and E. C. Raby (J. Biol. Chem., 1936, 113, 655—660).—HCN was determined by a photo-electric nephelometric method sensitive to 5×10^{-7}%. Part of the HCN which enters the leaves during fumigation is rapidly and permanently fixed, probably not entirely by aldehydes, sugars, or citral. HCN could not be recovered from the leaves by distillation with 2% tartaric acid owing to combination with some substance in the distillate. J. N. A.

Determination of the forms of calcium and oxalic acid in leaves of sugar-beet. A. P. Lebedeva and K. N. Potrchinok (Nauch. Zap. Sach. Prom., 1934, 11, Book 46—48, No. 8—10, 31—46).—A small portion of Ca in the leaves is not extractable by HCl. This fraction is higher in younger leaves. No H_2O- or AcOH-sol. Ca is present. The H_2O sol. C_2O_4'' varies in different parts of the leaf, is greater in the younger leaves, and is 1·5—2 times the quantity of CaC_2O_4 present. Ch. Abs. (*p*)

Subtropical fruit trees of Azerbaidshan. A. Kerimov (Bull. Appl. Bot. U.S.S.R., 1934, [iii], No. 5, 325—347).—Juice of cultivated pomegranates contains 11—19% of sugars and 0·4—6% of citric acid. Wild varieties have 12—18 and up to 8—9%, respectively. In olives the sugar content decreases as ripening progresses and again increases in over-ripe fruit. Changes in oil content are in the reverse order. The I val. of the oil increases with advancing ripeness. The oil content of almonds and pistachio nuts grown in different localities is recorded. Ch. Abs. (*p*)

Flavour of shōyu. II. K. Shōji (Bull. Inst. Phys. Chem. Res. Japan, 1936, 29, 166—170; cf. A., 1935, 1540).—A $CHCl_3$ extract after treatment with 10% NaOH affords hexoic acid, C_1 to C_6 primary alcohols, methyl-*n*-nonylcarbinol, and an unidentified product with the odour of shōyu. J. L. D.

Flavour of shōyu. III. K. Shōji (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 223—229).—An Et_2O extract of shōyu (not sterilised) yielded $CH_2Ph·CO_2H$, guaiacol, and Et vanillate. J. N. A.

Coumarins of root of *Heracleum sphondylium*, L.—See this vol., 860.

Kuromannin, shisonin, and nasunin.—See this vol., 861.

Constituents of bark of *Zanthoxylum americanum*.—See this vol., 859.

Oroxylin-*A*.—See this vol., 860.

Limonin, the bitter principle of orange kernels.—See this vol., 857.

Change of hesperidin content of peel of the mandarin orange during ripening: hesperidin content of juice, embedded fibre (white fibre on segments), and endocarp of ripened fruit. Y. Iwasaki (J. Agric. Chem. Soc. Japan, 1936, 12, 279—280).—Hesperidin (I) was determined by extraction of the dried substance with MeOH. The amount of (I) in the peel gradually decreased with advancing maturity; that in the dried white fibre of the segments was < that of the dried peel. Juice contained only a very small amount. J. N. A.

Preparation of sinigrin. S. Morell and K. P. Link (J. Biol. Chem., 1936, 114, 123—124).—Sinigrin cannot be obtained from *Brassica nigra* by Gadamer's method (A., 1897, i, 360), but good results can be obtained by the methods of Hérissey and Boivon (A., 1928, 207) and of Sandberg and Holly (A., 1932, 776). J. N. A.

Active principle of *Myrsine africana*, Linn. S. Krishna and B. S. Varma (J. Indian Chem. Soc., 1936, 13, 115—116).—Embelic acid (embelin) is extracted (yield 3%) by $CHCl_3$ from the fat-free berries; subsequent extraction with EtOH affords quercitol (I) (1%) and colouring matter. (I) is also isolable from the berries of *Embelia ribes*. H. B.

Constituents of *Evodia danielli*, Hemsl. S. Mayeda (J. Pharm. Soc. Japan, 1935, 55, 531—537).—The following are isolated from the $COMe_2$ extract: a *substance*, m.p. 80—80·5°, not reacting with BzCl or NH_2OH; *evodin*, $C_{26}H_{30}O_8$, m.p. 292—293°, $[\alpha]_D^{18}$ −129·4° in $CHCl_3$, also from *E. rutcacarpa*, Benth and Hook; *evodol*, $C_{29}H_{30(or\ 32)}O_{10}$, m.p. 281° (*Me* derivative, m.p. 279°); a terpenic oil. Ch. Abs. (*r*)

Presence of norstictic acid in the tree lichen *Lobaria pulmonaria* (L.), Hoffm. H. Schindler (Ber. deut. bot. Ges., 1936, 54, 240—246).—Production of red crystals with alkali is characteristic of norstictic (I) and α-methylethylsalazic as well as of salazic acid (A., 1934, 189, 891). (I) and stictic acid occur in *L. pulmonaria*. Asahina's diamine reaction is more sensitive than the KOH test. A. G. P.

Aromatic compounds of "Kasutorishochu." K. Shoji (Bull. Inst. Phys. Chem. Res. Japan, 1936, 15, 230—233; cf. B., 1933, 328).—Treatment of Kasutorishochu with NaOH yielded $CH_2Ph·CH_2·OH$ (*phenylurethane*, m.p. 79—80), octoic acid, and *p*-cresol. J. N. A.

Formation of potassium eugenoxide crystals during examination of plant ashes in violet oil. H. Tzoni (Mikrochem., 1936, 19, 208—213).—During use of violet oil as a medium for the microscopic investigation of the structure of the ash of plant tissues, crystals of K eugenoxide (I) form, especially along the leaf nerves. Highly siliceous tissues give no (I) crystals, owing to the formation of K_2SiO_3 during ashing. J. S. A.

Determination of carbohydrates in the leaves of *Euphrasia stricta* and of *Trifolium pratense*. N. Salageanu (Compt. rend. Soc. Biol., 1936, 121, 1531—1533).—Analytical vals. are given. R. N. C.

Hexose phosphates produced by higher plants. B. Tankó (Biochem. J., 1936, 30, 692—700).—The nature of the hexose phosphates produced by incubation of pea flours with added inorg. P is investigated. > 90% of the phosphorylated product consisted of 1 : 6-diphosphofructofuranose; the monophosphate complex was purified with brucine and was similar to the Robison ester but had a lower [α]; oxidation with Br left a non-aldose residue, possibly fructose 1-phosphate. Phosphohexokinase (A., 1935, 660) is present in pea flour and converts fructose 6-phosphate into a mixture of 62% of aldose and 38% of non-aldose esters. H. D.

Glucoside in *Pardanthus chinensis*, shekanin. Y. H. Wu (J. Chinese Chem. Soc., 1936, 4, 89—92).—Extraction of resin-free roots with 96% EtOH affords *shekanin*, m.p. 245—250° (*Ac* derivative, m.p. 182°, contains 4 Ac and 1 OMe groups), which is hydrolysed to a pentose and *shekangenin*, $C_{16}H_{16}O_8$, m.p. 257° (decomp.). J. L. D.

A new digitalic: *Menabea venenata*, Baillon. R. Hamet (Compt. rend. Soc. Biol., 1936, 121, 1327—1329).—The roots contain two glucosides with digitalin-like action; the name *menabein* is applied to the (apparently) more active of the two. R. N. C.

Gum from lemon trees. E. Anderson, F. H. Russell, and L. W. Seigle (J. Biol. Chem., 1936, 113, 683—690).—The purified gum, $[\alpha]_D^{25}$ +20·7°, is a compound of methylated uronic acid (2 mols.) + *d*-galactose (4 mols.) + *l*-arabinose (4 mols.)−H_2O (10 mols.). The gum, the structure of which is discussed, is not formed from pectic substances or hemicelluloses, but from sugars or polysaccharides in the inner part of the bark. J. N. A.

Separation of hydratopectin into calcium and magnesium pectinates and araban by means of water–alcohol–ether. T. K. Gaponenkov and V. N. Mimrikova (J. Appl. Chem. Russ., 1936, 9, 505—508).—Ca and Mg pectinates are pptd., whilst araban remains in solution, when 100 ml. of EtOH and 16·5 ml. of Et_2O are added to 50 ml. of 2% aq. hydratopectin. R. T.

Tea tannin. M. Nierenstein (Analyst, 1936, 61, 294).—The constitution of tea tannin is discussed in relation to the products of hydrolysis after methylation, and also to those resulting from the action of tannase (cf. B., 1922, 907A). E. C. S.

Constitution of tannins including those of tea and coffee. P. Maitland (Analyst, 1936, 61, 288—293).—The probable constitution of a no. of hydrolysable and condensed tannins is discussed. E. C. S.

Tannin from the Indian gooseberry (*Phyllanthus emblica*) with a protective action on ascorbic acid. M. Damodaran and K. R. Nair (Biochem. J., 1936, 30, 1014—1020).—A *tannin*, m.p. $> 360°$, containing gallic and ellagic acids and glucose, which inhibits the oxidation of ascorbic acid in air is prepared from the Indian gooseberry by extraction with MeOH and pptn. with EtOAc. A second *tannin*, decomp. 120°, without this inhibiting effect was also isolated. H. D.

Constituents of seeds of *Blepharis edulis*, Pers. I. J. B. Lal (J. Indian Chem. Soc., 1936, 13, 109—114).—Extraction of the oil-freed (C_6H_6) seeds with EtOH gives *dl*-allantoin (2·1%), a bitter glucoside (*blepharin*) (1·2%), $C_{16}H_{20}O_{11}$, m.p. 222° (softens at 220°), glucose, *o*-$C_6H_4(OH)_2$, tannins, and saponins. H. B.

Failure of iodine-starch reaction. E. Mangold and H. Jänsch (Sitzungsber. Ges. naturf. Fr. Berl., 1935, Feb., 35—40).—Potato that had been treated with saliva gave no blue colour but there was a yellow or brown coloration which could be removed by washing. Thereafter (I) produced a blue colour which could not be washed out. Nutr. Abs. (*m*)

Diastatic decomposition of intercellular cement. H. Colin and A. Chandun (Compt. rend., 1936, 202, 973—975).—Digestion of sugar-beet pulp at 15° with the digestive juice of *Helix* effects 50% greater decomp. of pectic substances than hot H_2O extraction, as measured by the reducing-sugar content. P. G. M.

Biochemical characteristics of variety in vegetables. B. A. Rubin and L. I. Naumova (Compt. rend. Acad. Sci., U.R.S.S., 1935, 4, 341—344; cf. A., 1935, 658).—In roots and leaves of early radishes the catalase (I), invertase (II), and amylase contents are $>$ those in late radishes, the differences being very pronounced in the cases of (I) and (II). Differences in wt. and sugar content between early and late varieties are also observed. W. McC.

Influence of climatic conditions on the resin content of the needles of coniferous trees. G. V. Pigulevski (J. Gen. Chem. Russ., 1935, 5, 1634—1638).—The resin content of the needles of different species of pine, larch, and fir is greatest in those growing in cold or temperate climates. R. T.

Properties of the secretion of *Primula obconica*. M. Hocquette (Compt. rend., 1936, 202, 1089—1091).—Differences (solubility in org. and inorg. solvents, colour reactions) between the fluid in the cells and the excreted matter may be due to the presence in the latter of fatty acids and/or neutral fats. W. McC.

Composition of the secretion of *Primula obconica*, Hance. M. Hocquette (Compt. rend., 1936, 202, 436—438).—The secretion of the hairs of *Primula obconica* probably contains saponosides or related compounds and phytosterols. H. G. M.

Composition of the oil of *Primula auricula*, L. A. Goris and H. Canal (Compt. rend., 1936, 202, 1351—1352).—Steam-distillation of the crushed and steeped roots of this plant give 0·8% of distillate consisting of pæonol and some *Me methoxyquinolcarboxylate*, an oil. The *acid*, m.p. 143°, therefrom gives 2 : 5-$C_6H_3(OH)_2{\cdot}CO_2H$, m.p. 200° [obtained from *p*-$C_6H_4(OH)_2$, CO_2, and $KHCO_3$ in glycerol at 180°], and is prepared from this acid by Me_2SO_4 (2 mols.) and boiling NaOH (2 mols.). R. S. C.

Essential oil of parasite-infested flower stems of marjoram. R. Salgues (Compt. rend. Soc. Biol., 1936, 121, 1074—1076).—Phenols, particularly thymol, in the oil are decreased by infection of the stems with *Eriophyces thomasi*. R. N. C.

Constituents of flowering dogwood (*Cornus florida*). C. E. Sando, K. S. Markley, and M. B. Matlack (J. Biol. Chem., 1936, 114, 39—45).—The fresh flowers and bracts (79·6 ≡ 16·3 kg. dry) of dogwood yielded 825 g. of Et_2O-sol. extract (I) and then a further EtOH-sol. extract (II). Ligroin (b.p. 30—60°) removed 330 g. from (I); after being shaken with 25% HCl, this was saponified by 3% KOH–EtOH, yielding palmitic and stearic (3 : 7), oleic, and some linolenic acids, a crude hydrocarbon, m.p. 62—62·5°, setting point 61·2—60·9° (probably a ternary mixture containing much $C_{29}H_{60}$), and a phytosterol, $C_{26}H_{43}{\cdot}OH$, $+H_2O$, m.p. 124° (acetate, m.p. 110—111°). The ligroin-insol. part of (I) gives ursolic acid. (II) yields inositol, scyllitol, campherol, gallic acid, and quercitin. R. S. C.

Chemical examination of seed of *Abies balsamea* (L.), Miller. S. R. Benson and H. N. Calderwood (J. Amer. Chem. Soc., 1936, 58, 523—525).—The seeds contain crude fibre 35·13, protein 9·42, ash 1·88, oleoresin (I) (extracted by 75% EtOH at room temp.) 19·1, and oil (by extraction of the (I)-free endosperm with light petroleum) 11·7% on a H_2O-free basis. The oil has d_{25}^{25} 0·9279, n_D^{25} 1·4783, f.p. —37°, acid val. 0·88, I val. (Hanus) 141, sap. val. 185·6, Ac val. 15·4, Reichert–Meissl val. 0·53, Polenske val. 0·21, contains 4·8% of unsaponifiable matter, and consists of the glycerides of stearic (small amount), oleic 33—40, linoleic (II) 54·6—59·7, and linolenic ($\Delta^{\theta\lambda\xi}$-octadecatrienoic) 3·1—5% acids. (II) appears to be a mixture of two isomerides, which when oxidised (aq. $KMnO_4$) give tetrahydroxystearic acids of m.p. 152° and 173°. H. B.

***Sium latifolium*, L., seeds.** G. V. Pigulevski and E. L. Karasik (J. Appl. Chem. Russ., 1936, 9, 284—286).—The seeds contain monoses 3·48, cellulose 21·31, protein 16·84, fatty oils 24·2, essential oils 7·01%. The fatty oil contains 2·2% of saturated acids; linoleic and oleic acids were also identified. R. T.

Constitution of certain nutshells. I. Seed-coat of *Bertolletia excelsa* (Brazil nut). J. G. Boswell (Biochem. J., 1936, 30, 971—976).—The fat of the shell was identical with that of the endosperm, and the hemicellulose and lignin were similar to those of other lignified tissues. The cellulose (furfuraldehyde yield high) was similar to that of peanut hull. H. G. R.

Unsaturated acid of kernel fat of "akarittom."—See this vol., 822.

Chemical constitution and biological properties of lipins in the carrot. D. Romoli-Venturi and A. Pugliese (Biochim. Terap. sper., 1935, **22**, 421—457).—The carrot, *Daucus carota*, contained: protein 1·2, fat 0·6, sugar reducing substances 6·5, non-N extractives 3·3, cellulose 1·6%. From the oil there were isolated a phospholipin with vitamin-*A* and -*D* reactions and containing Ca, N, and org. P, carotene, and material with the physicochemical properties of -*A* and -*E*. Nutr. Abs. (*m*)

Relation between ascorbic acid and carotenoids [in plants]. A. Giroud, A. R. Ratsimamanga, C. P. Leblond, Chalopin, and Rabinowicz (Bull. Soc. Chim. biol., 1936, **18**, 573—589; cf. this vol., 391).—With few exceptions, in plants where carotenoid compounds are present, significant quantities of vitamin-*C* are also found. A. L.

Lipins of wheat embryo. I. Fatty acids. II. Unsaponifiable fraction. B. Sullivan and C. H. Bailey (J. Amer. Chem. Soc., 1936, **58**, 383—390, 390—393).—I. EtOH-extracts of the fresh germ yield a mixture of carbohydrates containing sucrose, a little glucose, and an unidentified sugar (*acetate*, m.p. 229°, $[\alpha]_D^{27}$ $-$ 16·7° in $CHCl_3$). The oil (13·68% of germ) has d_{26}^{26} 0·9326, n_D^{20} 1·4800, acid val. 6·95 sap. val. 184, I val. (Rosenmund) 125, SCN-val. 84·7, Ac val. 16·7, Reichert–Meissl val. 0·77, Polenske val. 0·44, Hehner val. 89, ester val. 177·05, and contains 1·44% of sol. acids (as Pr^aCO_2H). Hydrolysis gives palmitic 11·76, stearic 3·05, lignoceric 1·19, oleic 28·14, α- 22·32 and β- 29·99 -linoleic, and α- 1·83 and β-linolenic acid 1·72%. Little or no fully saturated glyceride is present. Oxidation (1% $KMnO_4$, dil. NaOH) of the mixed unsaturated acids gives di-, α-, m.p. 155—155·5° (lit. 153—157°), and β-, m.p. 172·5°, -tetra-, and hexa-, m.p. 173° and 201—202°, -hydroxystearic acids.

II. The unsaponifiable matter (4% of oil) consists of about 70% of free (56·2%) and combined (43·8%) sterols (sitosterols, dihydrositosterol, and a sterol with $\not<$ 2 double linkings) and an almost N-free oil containing (cf. Drummond *et al.*, A., 1935, 418) polyene hydrocarbons, xanthophyll, and an alcohol. Determination of the unsaturation of sterols by I vals. (Hanus; Rosenmund) is untrustworthy. H. B.

Occurrence of ergosterol and vitamin-*D* in reindeer lichen. G. Blix and H. Rydin (Upsala Läkefören Forhandl., N.F., 1932, **37**, 333—340; Chem. Zentr., 1935, ii, 1398).—*Cladonia rangiferina*, L. Hoffm., contains small quantities of ergosterol, the content increasing in autumn. The vitamin-*D* content of the lichen is insignificant. R. N. C.

Sulphur-containing pigments of plant origin. P. Haas, T. G. Hill, and B. Russell-Wells (Nature, 1936, **137**, 783—784).—The blue compound formed on drying the actively growing shoots of *Mercurialis perennis* changes on keeping, or more rapidly on heating aq. solutions, into a red product which can be separated into a series of glucosidic pigments containing N and S. L. S. T.

Red gossypol. M. Podolskaja (Biochem. Z., 1936, **284**, 401—411).—Cotton seeds contain, in addition to a yellow pigment (I), a red cryst. *compound* (II), $C_{30}H_{30}O_8$, containing 2 $\cdot CO_2H$ groups; (I) and (II) are distinguished by pleochroism and extinction and absorption spectra but both yield the same derivative with AcOH and NH_2Ph. In EtOH, (II) changes to (I) whilst $CHCl_3$ solutions are relatively stable (cf. B., 1935, 732; Schmid and Margulies, A., 1935, 984). F. O. H.

Pigment of the flowering currant (*Ribes sanguineum*, vars. *splendens* and *atrosanguineum*). T. J. Nolan and T. G. Brady (Proc. Roy. Irish Acad., 1936, **43**, B, 1—12).—The pigment of these two varities is isolated and identified as antirrhinin (keracyanin) (cf. A., 1930, 967). E. W. W.

Mandarin pigment. II. L. Zechmeister and P. Tuzson (Z. physiol. Chem., 1936, **240**, 191—194; cf. A., 1934, 121).—The fruit contains carotene, cryptoxanthin in the proportion 1 : 10—25, xanthophyll, and probably violaxanthin and zeaxanthin. W. McC.

Carotenoids of fresh-water algæ. I. Euglenarhodone and other carotenoids of a red *Euglena*. J. Fischer (Z. physiol. Chem., 1936, **239**, 257—269; cf. Kylin, A., 1927, 703).—In addition to chlorophyll-*a* and -*b*, β-carotene, esterified zeaxanthin and lutein, xanthophyll, fatty acids (palmitic), and glycerol, *E. heliorubescens* contains two esters of *euglenarhodone* (I), $C_{40}H_{48}O_4$, m.p. 227—228° (corr.) [*dioxime* (II) (absorption max. at 512 mμ in C_5H_5N); *tetraoxime*]. (I), which is probably 4 : 6 : 4′ : 6′-tetraketo-β-carotene, exhibits an absorption band at 480—535 mμ (max. at 505 mμ) in C_5H_5N and when pure is very stable in air. (I) and (II) yield salts with heavy metals. W. McC.

Awobanin and awobanol.—Sed this vol., 860.

Colouring matter in the wood of "Hinoki" tree. I.—See this vol., 857.

Tanganyika arrow poisons.—See B., 1936, 475.

Chemical investigation of Indian medicinal plants. V. *Cryptocryne spiralis*. S. N. Chakravarti and T. S. Kuppuswamy (J. Annamalai Univ., 1936, **5**, 269—270).—No org. active principle is detected in the root of this plant. E. W. W.

Detection of scopoletin in gelsemium and belladonna roots. R. Fischer and H. Ehrlich (Arch. Pharm., 1936, **274**, 268—273).—The method of isolating scopoletin from gelsemium and its extract is improved. Micro-sublimation at 125°/12 mm. (2—3 mm. distance) gives stable, m.p. 204—205° (mostly six-sided; angle 137°), and unstable *forms*, m.p. 193—195° (often twinned; shape variable). Partly purified extracts, but not the powdered roots, give recognisable sublimates. R. S. C.

"Lofout," a Saharan lily containing colchicine. E. Perrot (Compt. rend., 1936, **202**, 1088—1089).—All parts of the plant (*Androcymbium gramineum*) contain colchicine (seeds 0·37, bulbs, 0·29, flowers 0·1%). W. McC.

Alkaloid content of infusions and decoctions of seeds of *Lupinus albus*. D. Torrisi (Boll. Soc. ital. Biol. sperim., 1935, **10**, 807—809).—Prolonged roasting slightly reduces the lupanine (I) content of the seeds, and, by increasing the imbibing power of the seeds, increases the quantity of (I) that can be extracted by decoction or infusion. R. N. C.

Presence of alkaloids in *Sambucus*. H. Yardin (Compt. rend. Soc. Biol., 1936, **122**, 155—156).—Choline and other bases giving alkaloid reactions are present in extracts of the bark; cicutine is absent. R. N. C.

Nicotinamide methiodide.—See this vol., 862.

Alkaloids of white hellebore.—See this vol. 870.

Alkaloids of *Holarrhena antidysenterica*. IV.—See this vol., 870.

Amino-acid content of root nodules. A. I. Virtanen and M. Tornianen (Suomen Kem., 1936, **9**, B, 13—14).—Proteins of nodules yielded tryptophan, arginine, tyrosine, aspartic acid (I), and $(NH_2)_2$-acids. Excretion of (I) and lysine by nodules is not due to fission of protein. These NH_2-acids represent primary products of N fixation. A. G. P.

Non-protein-nitrogen of pulses. K. Bhagvat and M. Sreenivasaya (Current Sci., 1936, **4**, 651—652).—Differentiation of the non-protein-N indicates that *P. mungo* is very rich in proline, whilst *P. aconitifolius* (I) and *C. arietinum* are rich in arginine and arginine-like compounds. The % of dicarboxylic N in (I) is high. F. A. A.

Constituents of mulberry leaves, especially proteins. XI. Distribution of amino-acids in leaf proteins. XII. Solubility of leaf proteins and its application. Y. Kishi (J. Agric. Chem. Soc. Japan, 1936, **12**, 348—362, 363—378; cf. A., 1935, 1146).—XI. The N distribution of the protein sol. in 60% EtOH containing 0·3% of NaOH is examined. This fraction constitutes the major portion of the protein in dried leaves and is distinct from globulin, glutelin, and albumin present.

XII. The N distribution of the H_2O-sol. protein of dried leaves differs from that of fresh leaves. The latter consists largely of the alkaline-EtOH-sol. protein obtained from dried leaves. Fractionation of the proteins with other solvents is examined. A. G. P.

Globulin from the cashew nut (*Anacardium occidentale*). M. Damodaran and T. G. Sivaswamy (Biochem. J., 1936, **30**, 604—608).—The fat-free seed yields 17—18% of a globulin, *anacardein* (N 19·3, S 0·75—0·78%; P nil; Molisch test negative). W. O. K.

Proteins of Indian foodstuffs. VII. Globulins of the aconite bean (*P. aconitifolius*, Jacq.). VIII. Heat-coagulation of globulins from *Vigna catiang*, Walp., and *P. aconitifolius*, Jacq. K. Bhagvat. **IX. Digestibility of globulins from cow-pea and aconite bean.** K. Bhagvat and M. Sreenivasaya (J. Indian Inst. Sci., 1935, **A**, **18**, 137—144, 145—151; 1936, **A**, **19**, 9—18).—VII. The globulins (I) of aconite bean were fractionated by $COMe_2$ and $(NH_4)_2SO_4$ pptn. and by a dilution technique. $CHCl_3$ extracted more org. P than other lipin solvents.

VIII. The (I) were fractionated by heat-coagulation.

IX. The tryptic digestion of (I), measured by direct N determinations and by a dilatometric technique which gave good agreement, was much slower than that of caseinogen. Preliminary treatment of (I) with pepsin increased the rate of digestion. The viscosimetric determination of digestibility was obscured by ppt. formation. H. D.

Methylene-blue technique for permanent preparations. E. C. Cole (Stain Tech., 1936, **11**, 45—47).—Tissues stained intravitally with methylene-blue are best fixed with $(NH_4)_2MoO_4$, washed in H_2O, and dehydrated with EtOH–$Bu^{\alpha}OH$ (1 : 1) followed by pure BuOH and finally by Me salicylate–xylene (1 : 4). W. O. K.

Physical chemistry of silver staining. L. Zon (Stain Tech., 1936, **11**, 53—67).—Silk fibres in aq. NH_3–AgOH adsorb Ag, but the amount of Ag deposited in the fibres on addition of CH_2O is > that originally adsorbed. It is concluded that during Ag staining actual deposition of Ag takes place in the tissues as opposed to simple reduction of Ag already adsorbed. Various factors influencing Ag reduction, *e.g.*, adsorption of AgOH and NH_3, affinity of Ag for proteins, and the protective power of the gel structures, are discussed and the conclusions reached are applied to modified methods of Ag staining. W. O. K.

[Differential] staining with safranine and fast-green FCF. J. A. Moore (Stain Tech., 1936, **11**, 69—70). W. O. K.

Feulgen reaction. J. A. de Tomasi (Stain Tech., 1936, **11**, 70).—Improvements in the Feulgen staining reaction (cf. A., 1924, i, 905) are described. W. O. K.

Micro-extraction apparatus for determining alcohol–ether-soluble lipins. J. Erdős and L. Pollak (Mikrochem., 1936, **19**, 245—247).—The material is supported on a filter cone beneath the reflux condenser. J. S. A.

Sensitivity and stability of the nickel nitroprusside reaction for reduced glutathione. D. Zimmet and H. D. Ferrière (Arch. Sci. phys. nat., 1936, [v], **18**, Suppl., 44—48).—When one or two drops of a solution containing $NiCl_2$ (5 g.) and $Na_2Fe(CN)_5NO$ (0·5 g.) in H_2O (100 c.c.) are added to a solution of reduced glutathione a rose-violet ppt. is formed, a greenish turbidity being obtained with distilled H_2O. The reaction is highly sensitive, being positive with 0·25 p.p.m., and is not given by $COMe_2$, creatinine, or cysteine. W. O. K.

Determination of paraldehyde (A) in the tissues and fluids after intravenous injection of this substance, (B) in the respiratory air of paraldehyde-anæsthetised animals. I. I. Nitzescu, I. D. Georgescu, and D. Timus (Compt. rend. Biol., 1936, **121**, 1657—1659, 1660—1661).—(A) Paraldehyde (I) is determined by boiling the tissue in 10% H_2SO_4, the depolymerised MeCHO being absorbed in aq. $NaHSO_3$, excess of which is determined iodometrically. (I) injected into the dog is stored in most organs, particularly the heart, but a large quantity remains in the blood and is eliminated in the urine and expired air.

(B) The expired air is passed through hot 10% H_2SO_4 to depolymerise (I), and then through aq. $NaHSO_3$ in which MeCHO is absorbed and determined. R. N. C.

Determination of fats in biological material. P. A. SESHAN (Indian J. Vet. Sci., 1935, **5**, 355—363).—With ragi straw, earthnut cake, and dried fæces, extraction with Et_2O or light petroleum for 16 hr. is inadequate. The extract in the later stages differs materially (*e.g.*, in sap. val. and fatty acid content) from that obtained in the early stage of the extraction. The alkali hydrolysis method also gives unsatisfactory results owing to its destructive nature. NUTR. ABS. (*m*)

Enzymic histochemistry. XVII. Micro-determination of nitrogen. M. LEVY (Z. physiol. Chem., 1936, **240**, 33—42).—A method, applicable to approx. 0·1 mg. of N and based on digestion of the tissue-extract with H_2SO_4–K_2SO_4–Se and subsequent nesslerisation, is described. F. O. H.

Adsorption of nitrogenous substances from aqueous solutions. D. ACKERMANN and H. G. FUCHS (Z. physiol. Chem., 1936, **240**, 198).—Lloyd's reagent (in 5% H_2SO_4) is as effective as, and in some ways preferable to, phosphotungstic acid as an adsorbent for substances containing N. Adsorbed material is recovered by long-continued elution with aq. $Ba(OH)_2$. W. McC.

Micro-determination of uric acid.—See this vol., 873.

Microchemical detection of arsenic in forensic investigations. A. MARTINI and B. BERISSO (Mikrochem., 1936, **19**, 181—182).—Animal tissues etc. are decomposed with alkaline H_2O_2. The solution is acidified with HCl, and treated with conc. aq. NaI + a drop of quinoline. In presence of $> 4 \times 10^{-10}$ g. of As a microscopically characteristic yellow cryst. ppt. is obtained. Alternatively, 20% aq. CsCl, saturated aq. Na_2HPO_4, and C_5H_5N are added, giving a characteristic ppt. J. S. A.

Determination of boron in soils and plants. E. V. BOBKO and T. V. MATVEEVA (J. Appl. Chem. Russ., 1936, **9**, 532—540).—Bertrand and Agulhon's method (A., 1914, ii, 217) is preferred. The B content of moist is $<$ that of dry soils. The B content of apple leaves is $<$ that of the blossoms, in which the stigmata are richest in B. The B content of plants may be increased 3—4-fold by raising the B content of the nutritive solution. R. T.

Determination of halogen absorption of oils.—See B., 1936, 461.

Bromine in the body. H. UCKO (Biochem. J., 1936, **30**, 992—1000).—A colorimetric method for determination of Br and of the Br and Cl content of various tissues (normal and after Br intake) is described. H. G. R.

Determination of bromine. G. E. BATRAK (Med. exp. Ukraine, 1935, No. 2, 100—104).—In the colorimetric method using Schiff's reagent, the depth of colour of the lilac rings developing when drops of aq. Cl_2 are added is measured by ocular observation. NUTR. ABS. (*m*)

Determination of iodine in biological material. G. J. FASHENA and V. TREVORROW (J. Biol. Chem., 1936, **114**, 351—355; cf. A., 1935, 1182).—Reduction of IO_3' by HPO_3' is increased by dilution of the reaction mixture. H. D.

Ionisable iron in foods. L. SHACKLETON and R. A. McCANCE (Biochem. J., 1936, **30**, 582—591).—The ionisable Fe in various foodstuffs, determined by the 2 : 2′-dipyridyl method and expressed as a % of the total Fe, appears more const. and characteristic of the foodstuff than the total Fe. Cereals contain 75—100, vegetables and fruits 50—100, beef and mutton 10—25, other flesh foods > 25, most white fish 100, and herring, mackerel, and sardines about 60% of their Fe in ionised form. W. O. K.

Micro-determination of potassium in substances of biological origin. A. CAHEN (Bull. Soc. chim., 1936, [v], **3**, 640—643).—The substance is oxidised by HNO_3–$HClO_4$ and K obtained as K_2PtCl_6 by evaporation with $PtCl_4$. K_2PtCl_6 is reduced by H_2, and the KCl titrated by standard methods. The error is $< 2\%$. E. S. H.

Micro-determination of potassium.—See this vol., 812.

Colorimetric determination of inorganic sulphate in serum and urine. T. V. LETONOFF and J. G. REINHOLD (J. Biol. Chem., 1936, **114**, 147—156).—A method based on the colour-producing reaction between benzidine sulphate and Na β-naphthoquinone-4-sulphonate is described. PO_4''' and proteins are removed simultaneously by uranyl acetate prior to the analysis. The inorg. S of normal human serum is approx. 1·04 mg. per 100 c.c. Additional SO_4'' is liberated when serum is treated with $CCl_3{\cdot}CO_2H$. SO_4'' added to serum is rendered partly non-precipitable by benzidine. J. N. A.

Determination of sulphur for sulphur-balance experiments with cattle and sheep. F. J. WARTH and T. S. KRISHNAN (Indian J. Vet. Sci., 1935, **5**, 210—215).—The method, which is applicable to urine, fæces, and foodstuffs, consists in oxidation with HNO_3 followed by fusion of the evaporated filtrate with NaOH in a Ag basin. NUTR. ABS. (*m*)

Sulphur metabolism. Sulphur and protein metabolism in infants and children. A. BLAZSO (J. Physiol. Path. gén., 1935, **33**, 1076—1092).—S is determined in urine, fæces, serum, and milk, by oxidising with fuming HNO_3 and removing phosphates with $Ca(OH)_2$. After neutralisation, excess of $BaCrO_4$ is added and then $Ca(OH)_2$ to ppt. the excess. The H_2CrO_4 liberated is determined colorimetrically in the filtrate with *s*-diphenylcarbazide. NUTR. ABS. (*m*)