BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JUNE, 1935.

BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

General, Physical, and Inorganic Chemistry.

Structure of the hydrogen lines. K. Bechert and J. Meixner (Ann. Physik, 1935, [v], **22**, 525—536).—Theoretical. The difference between the observed splitting of the lines of the Balmer series for H and that given by Sommerfeld's theory is discussed. No difference between the lines for H and D can be found experimentally (cf. this vol., 271). The mass correction of Darwin can be derived by wave mechanics. The distance between the intensity max. of the fine structure is not changed by the hyperfine structure. A. J. M.

Extension of ultra-violet wave-length limit. H. Alfvén and V. H. Sanner (Nature, 1935, **135**, 580—581).—The short-wave limit of the ultra-violet has been extended to 21 Å. by means of a spark discharge between C and C+$LiNO_3$ electrodes. L. S. T.

Calculation of band constants for the second positive nitrogen group. A. Guntsch (Ann. Physik, 1935, [v], **22**, 657—661).—Calculation of the band consts. (B and D) for the second positive N group gives vals. disagreeing with those of Büttenbender and Herzberg (this vol., 271). It is emphasised that the form of the function $\phi(J)$ is not known. A. J. M.

[Calculation of band constants for the second positive nitrogen group.] G. Herzberg (Ann. Physik, 1935, [v], **22**, 662).—The introduction of $(J+\frac{1}{2})$ in the expression for $\phi(J)$ gives results in agreement with experiment. A. J. M.

Stark effect in molecular spectra of nitrogen, carbon dioxide, and hydrogen. W. Rave (Z. Physik, 1935, **94**, 72—84). A. B. D. C.

Forbidden O I lines in the spectrum of *Nova Herculis* 1934. W. Grotrian and W. Rambauske (Naturwiss., 1935, **23**, 248).—The spectrum has a strong emission line at 6300 and two weaker ones at 6362·2 and 5576·5 Å., which are the forbidden lines of the O I spectrum, $2p^1D_2-2p^1S_0$, $2p^3P_2-2p^1D_2$, and $2p^3P_1-2p^1D_2$. All these increased considerably in intensity during the early months of 1935. A. J. M.

Wave-length table for the vacuum spark spectrum of fluorine. B. Edlén (Z. Physik, 1935, **94**, 47—57). A. B. D. C.

Electronic excitation function of the metastable s_5 level of neon. J. M. W. Milatz and L. S. Ornstein (Physica, 1935, **2**, 355—362).—The excitation function (I) of the metastable s_5 level of Ne was determined by measuring the absorption (1·5%) of light of λ 6402. The methods by which metastable atoms could be produced are considered, and it is shown that collisions of the second kind, bringing atoms from the s_4 to the s_5 level, and excitation by way of the p_9 level could not account for the no. of metastable atoms produced. It is concluded that the optical (I) measured is also the electrical (I) for the s_5 level. A. J. M.

Transition probabilities for the *D* lines of sodium from absolute intensity measurements, the dissociation of sodium salts, and the half width of the *D* lines in the luminous gas-air flame. R. Minkowski, H. G. Müller, and M. Weber-Schäfer (Z. Physik, 1935, **94**, 145—171).—Na salts are only 30—80% dissociated in the ordinary gas flame, and deviations from thermal equilibrium are pronounced. A. B. D. C.

Transition probability for $2P$—$1S$ of sodium from absolute intensity measurements of flames. R. Minkowski and M. Weber-Schäfer (Z. Physik, 1935, **94**, 172—175).—The results of Held and Ornstein (A., 1932, 979) are discussed. A. B. D. C.

Mechanical moment of the cobalt nucleus. H. Kopfermann and E. Rasmussen (Z. Physik, 1935, **94**, 58—67).—This moment is 7/2. A. B. D. C.

Deep configurations of cobalt. H. H. Marvin (Physical Rev., 1935, [ii], **47**, 521—526).—Term vals. for Co I and g-factors for the Zeeman effect in intermediate coupling are calc. N. M. B.

Zeeman effect in the arc spectrum of cobalt. F. L. Roth and P. F. Bartunek (Physical Rev., 1935, [ii], **47**, 526—531).—Zeeman patterns for 151 lines in the range λλ 3200—6500 are tabulated. Calc. and experimental g-factors for 100 terms are compared for LS and intermediate coupling. N. M. B.

Spectrum of selenium. V. Structure of Se II. S. G. Krishnamurty and K. R. Rao (Proc. Roy. Soc., 1935, **A**, **149**, 56—70; cf. A., 1934, 935).—About 200 lines between 8000 and 450 Å. ascribed to Se II have been classified as belonging to the quadruplet and doublet systems. The largest term, $4p^4S_{1\frac{1}{2}}=174{,}994$ cm.$^{-1}$, gives for ionisation potential 21·6 volts. L. L. B.

Effect of magnetic field on the fluorescence of diatomic molecules of selenium. J. Genard

(Physica, 1935, **2**, 328—334).—The effect of a strong magnetic field on the resonance radiation of Se_2 vapour was determined. The effect varies from term to term. A. J. M.

Intensity measurements with a reflexion echelon. J. H. GISOLF and P. ZEEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 225—229).—The relative intensities of the hyperfine structure components of the Cd line 4678 Å., $^3P_0$—$^3S_1$, have been measured. R. S. B.

Hyperfine structures in La III. Nuclear magnetic moment of lanthanum. M. F. CRAWFORD and N. S. GRACE (Physical Rev., 1935, [ii], **47**, 536—538).—Hyperfine structure separations and intensities in the resonance lines 3517 and 3172 Å. of La III were measured. The calc. moment is 2·8 nuclear magnetons. N. M. B.

Zeeman effect in the tungsten spectrum. M. A. CATALÁN and F. POGGIO (Anal. Fís. Quím., 1934, **32**, 255—270).—After applying corrections to Being's results (A., 1927, 491), vals. are obtained in accordance with Jack's data (A., 1909, ii, 280). D. R. D.

Electrical and photo-technical properties of high-pressure mercury-vapour discharges. B. N. KLJARFELD and E. S. PLOKHOTZKI (J. Tech. Phys. U.S.S.R., 1934, **5**, 796—803).—The dependence of spectral distribution and intensity on discharge characteristics was measured. CH. ABS. (*e*)

Characteristics of Pb I, II, III, IV lines revealed in instantaneous spectrograms. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1935, **11**, 43—46).—A qual. discussion of the principal features of the lines. N. M. B.

Lines or bands in the spectrum of the night sky. J. V. KARANDIKAR (Indian J. Physics, 1935, **9**, 245—250).—Data and those obtained by other investigators are tabulated. λλ 5577, 6300, and 6360 are attributed to at. O; the others are not identified. N. M. B.

Classification of stellar spectra. H. N. RUSSELL, C. H. P. GAPOSCHKIN, and D. H. MENZEL (Astrophys. J., 1935, **81**, 107—118). L. S. T.

Photochemical processes in comets. K. WURM (Chem.-Ztg., 1935, **59**, 345—347).—The origin of the mols. present in the atm. of various parts of a comet, as indicated by a study of its spectrum, is discussed. A. J. M.

Distribution of nuclear mechanical moments. S. TOLANSKY (Nature, 1935, **135**, 620—621).—The difference in the distributions of nuclear mechanical moments of odd at. no. atoms (*A*) and of even at. no. atoms (*B*) is marked. Although class *B* is only one third as numerous as class *A*, yet more spins of ½ occur in *B* than in *A*. High vals. for nuclear moments are improbable in class *B*, whilst class *A* tends to show that 3/2 and 5/2 are very stable vals. when there is an odd nuclear proton. L. S. T.

Ion distribution during the initial stages of spark discharge in non-uniform fields. C. D. BRADLEY and L. B. SNODDY (Physical Rev., 1935, [ii], **47**, 541—545).—A Wilson cloud-chamber method is described for a direct study of ion distribution in the gap space, before visual or photographic luminosity has developed, with potential impulse $< 10^{-7}$ sec. duration. N. M. B.

Optical terms calculated with Fermi's statistical potential. E. HELLMIG (Z. Physik, 1935, **94**, 361—368). A. B. D. C.

Isotope effect in band spectra of hydrides and deuterides. L. HULTHÉN (Nature, 1935, **135**, 543).—Theoretical. L. S. T.

[Wave-mechanical theory of the Stark effect and atomic interactions.] C. W. OSEEN (Ark. Mat. Astr. Fys., 1934, **A**, **25**, No. 2, 14 pp.; Chem. Zentr., 1934, ii, 3221).—The use of certain conceptions of classical physics in wave mechanics is criticised. H. J. E.

Geiger counter applied to light measurements. B. STURM (Z. Physik, 1935, **94**, 85—103). A. B. D. C.

Electric arc. H. PLESSE (Ann. Physik, 1935, [v], **22**, 473—499).—The conditions obtaining in the electric arc struck between various elements were investigated. A. J. M.

Distribution of chief colours in the spectrum. H. P. J. VERBEEK and M. L. BAZEN (Physica, 1935, **2**, 380—382).—The names given by 100 persons to light of 21 different λ are recorded. A. J. M.

Precision measurements of the $K\alpha_{1,2}$ doublets of some of the lighter elements. P. HAGLUND (Z. Physik, 1935, **94**, 369—376).—Results are given for Al, Si, and S. A. B. D. C.

Intensity ratios of the fluorescent *X*-ray emission lines in the *L* region and their dependence on the voltage. H. HIRST and E. ALEXANDER (Phil. Mag., 1935, [vii], **19**, 918—927).—Intensity ratios (I) of *L* emission lines of W, Tl, and U excited by *X*-rays and by cathode rays have been determined. (I) of lines originating from the same electron level are independent of voltage. (I) of other lines increase to a max. at 3—4 times the excitation voltage. R. S.

***L* spectrum of mercury.** (MLLE.) Y. CAUCHOIS (Compt. rend., 1935, **200**, 1194—1196).—The λλ of the *L*-series *X*-ray lines of Hg have been redetermined and the results compared with previous data. J. W. S.

Efficiency coefficients, intensity ratios, and absorption probabilities in the *L* series of the heavy elements. H. KÜSTNER and E. ARENDS (Ann. Physik, 1935, [v], **22**, 443—472).—The characteristic *L*-radiation for monochromatic *X*-rays of Ta, W, Ir, Pt, Au, Pb, and Bi was investigated. The efficiency coeffs., u_1, u_2, and u_3, were determined for the three *L*-levels. u_1 and u_3 increase with increasing at. no., but u_2 decreases. The intensity ratios of the line groups at the various *L*-band edges were determined. With increasing at. no. there is an increase in the ratio $E_3 : E_2$, but a decrease in $(E_2+E_3) : E_1$. The absorption probabilities (I) were also determined. The ratio of (I) in the L_2+L_3 levels to that in L_1 increases with the distance from the L_1 edge, reaches a max., and then rapidly decreases, disagreeing with Schur's theory (A., 1930, 391). A. J. M.

M series of element 91, protoactinium. W. C. Pierce and A. V. Grosse (Physical Rev., 1935, [ii], **47**, 532—533).—Data and identifications for 14 lines are tabulated. Measurements for the corresponding *M* lines of U are given. N. M. B.

Disintegration of a monatomic thorium film on a tungsten cathode in a discharge in mercury vapour. N. Morgulis and M. Bernadiner (Physikal. Z. Sovietunion, 1934, **6**, 309—311).—The min. crit. potential of the ion to cause disintegration is calc. Ch. Abs. (*e*)

Temperature ionisation of a gas. II. General theory and relation between temperature and pressure ionisation. M. Sugita (Proc. Phys.-Math. Soc. Japan, 1934, **16**, 401—413).—Theoretical. Ch. Abs. (*e*)

Behaviour of electrons in chlorine. V. A. Bailey and R. H. Healey (Phil. Mag., 1935, [vii], **19**, 725—746; cf. A., 1934, 825).—A new method of investigation is described, in which the motion of electrons (I) in Cl_2 is studied by observations on mixtures of Cl_2 with He or CO_2. The probability of (I) becoming attached to a mol. with which it collides, and the mean free path of (I), are max. when the mean electronic velocity (u) is about $7{\cdot}7\times10^7$ cm. per sec. The mean proportion of its own energy lost by (I) on collision with a mol. also varies with u, and shows parallelism with the optical absorption. The views of Franck and others are criticised. F. L. U.

Scattering absorption of electron rays. A. Recknagel (Z. Physik, 1935, **94**, 356—360).—Theoretical. A. B. D. C.

Production of [electron] pairs by collisions of particles. L. Nordheim (J. Phys. Radium, 1935, [vii], **6**, 135—136).—Mathematical. N. M. B.

Production of electrons and positrons by collision of two particles. L. Landau and E. Lifschitz (Physikal. Z. Sovietunion, 1934, **6**, 244—257).—Theoretical. Ch. Abs. (*e*)

Production of protons by bombardment of palladium with electrons. R. Kollath (Z. Physik, 1935, **94**, 397—407).—A study of the production of protons from H_2 absorbed in Pd shows that it does not correspond with ejection from a solid surface but with electron collision in a H_2 atm. A. B. D. C.

Negative ions of iodine. I. Probe measurements. J. L. Spencer-Smith (Phil. Mag., 1935, [vii], **19**, 806—823).—Measurements by means of a Langmuir probe show that the concn. of negative ions approx. = that of the positive ions and $\gg$ that of the free electrons, when the pressure of I_2 vapour is between 0·1 and 0·5 mm. The effect of I_2 on the glow discharge in He has also been studied. F. L. U.

Negative ions of iodine. II. Ion beams. J. L. Spencer-Smith (Phil. Mag., 1935, [vii], **19**, 1016—1027; cf. preceding abstract).—A beam containing the ions I', I_2', and I_3' obtained from the glow discharge in I_2 has been subjected to magnetic analysis. The presence of I'', I^*, I_2^*, and I_3^* in a similar beam of positive ions has been established, and the distribution of both types of ions in the discharge determined. Probability data are given for the collision of electrons and negative ions with neutral I_2 mols. R. S.

Production of ion currents in high vacuum with the aid of a magnetic field. A. A. Slutzkin, S. I. Braude, and I. M. Vigdorchik (Physikal. Z. Sovietunion, 1934, **6**, 268—279). Ch. Abs. (*e*)

New ion sources for mass spectroscopy. A. J. Dempster (Nature, 1935, **135**, 542).—Positively-charged atoms are formed by sparks between solid electrodes in a high vac. The spark is coupled inductively to a high-frequency oscillating spark circuit. Abundant ions, many multiply-charged, are obtained from Pt, Au, W, Sn, Cu, Ni, Fe, Al, C, Be, and Li. L. S. T.

Masses of some light atoms determined by a new method. F. W. Aston (Nature, 1935, **135**, 541).—Mass differences of some of the lighter atoms have been determined by resolving and measuring in mass spectra naturally-occurring doublets which represent small residual differences between the atoms and mols. concerned. Provisional vals. for the masses relative to O^{16} obtained from the doublets D,H_2, He,D_2, C^{++},D_3, and O,CH_4 are H 1·0081, D 2·0148, He 4·0041, and C 12·0048. They are in better accord with the masses deduced from energy changes during artificial disintegrations. L. S. T.

Comparison of *X*-ray and γ-ray dosage. L. S. Taylor and F. L. Mohler (Science, 1935, **81**, 318—319).—Abs. measurements of the ionisation produced in CS_2 by γ-rays are recorded. L. S. T.

Radioactivity of potassium and rubidium. F. H. Newman and H. J. Walke (Phil. Mag., 1935, [vii], **19**, 767—773; cf. this vol., 275).—Arguments in favour of the long-life activity of K being due to $_{19}K^{40}$, formed by bombardment of $_{19}K^{39}$ with neutrons of low energy, are given. Similar arguments indicate $_{37}Rb^{86}$ as the active Rb isotope. F. L. U.

Radioactivity of rubidium. F. H. Newman and H. J. Walke (Nature, 1935, **135**, 508).—The effects observed when Rb, Yt, and Sr are bombarded with neutrons support Klemperer's view that $_{37}Rb^{86}$ is the source of the natural β-radioactivity of Rb. L. S. T.

Radioactivity of the rare earths. H. J. Walke (Phil. Mag., 1935, [vii], **19**, 878—886).—The results of Aston (A., 1934, 1150) are considered in relation to the author's theory of isotope synthesis (this vol., 427). R. S.

Expression for Bragg curves for α-particles from radioactive substances. M. Francis (J. Phys. Radium, 1935, [vii], **6**, 108—113).—Ionisation curves which, for certain α-rays, cannot be determined experimentally can be deduced from known curves for other substances. The method is illustrated for the U curve from that for Po. N. M. B.

Differential ionisation of single polonium α-rays in air and scattering of their range. H. Schulze (Z. Physik, 1935, **94**, 104—133). A. B. D. C.

β- and γ-Rays of radium-*D*. J. A. Gray (Canad. J. Res., 1935, **12**, 408).—There is evidence that every atom of Ra-*D* emits a γ-ray on disintegration. The

total no. of β-rays emitted in 100 disintegrations should be 100 primary, 96 secondary, and about 100 tertiary. J. W. S.

Photo-electric absorption of γ-rays in heavy elements. H. R. Hulme, J. McDougall, R. A. Buckingham, and R. H. Fowler (Proc. Roy. Soc., 1935, **A**, **149**, 131—151).—Results obtained by various authors for the photo-electric effect in H-like atoms are co-ordinated, and a method is developed for finding σ_K, the photo-electric absorption coeff. for the K shell, which is valid for all vals. of the at. no. and where $h\nu_0 \sim mc^2$. Graphs are constructed giving the photo-electric absorption per atom for various elements in the range $h\nu_0 > 0{\cdot}7mc^2$. L. L. B.

Interaction of hard γ-rays with atomic nuclei. C. Y. Chao and T. T. Kung (Chinese J. Physics, 1934, **1**, 56—65).—The no. of counts with a Geiger–Müller counter using Th-C'' γ-rays has been compared for Pb and Al walls, with evidence for the interaction of the γ-rays with Pb nuclei, producing positive and negative electrons. R. S. B.

Artificial excitation of nuclear γ-radiation. E. Kara-Michailova (Sitzungsber. Akad. Wiss. Wien, 1934, IIa, **143**, 1—9; Chem. Zentr., 1934, ii, 3588).—Intense bombardment with α-particles from Po produced penetrating nuclear γ-radiation from Be, B, N, Al, Na, and Mg, but not from C, O, Si, P, S, Cl, and K. H. J. E.

Scattering of neutrons by protons. H. A. Bethe and R. Peierls (Proc. Roy. Soc., 1935, **A**, **149**, 176—183).—Theoretical. The cross-section and angular distribution are calc. for the scattering of neutrons by protons. The result depends only on the known binding energy of the diplon, and is independent of the law of force assumed between neutron and proton. The scattering is almost isotropic for neutron energies up to 4×10^4 kv. L. L. B.

Transmutation of heavy hydrogen investigated by the cloud-track method. P. I. Dee and C. W. Gilbert (Proc. Roy. Soc., 1935, **A**, **149**, 200—209).—By passing a beam of artificially accelerated $_1D$ ions into a gas mixture containing D_2, the $_2He^3$ nuclei produced in the reaction $_1D+{}_1D \longrightarrow {}_2He^3+{}_0n^1$ have been detected in the expansion chamber. The range of the $_2He^3$ nucleus for zero bombarding energy is $4{\cdot}3 \pm 0{\cdot}2$ mm. The energy of the neutrons $= 1{\cdot}8 \pm 0{\cdot}2 \times 10^6$ e.v. The results are in agreement with the application of the conservation of momentum to the process assumed, and a val. of $1{\cdot}008 \pm 0{\cdot}0004$ is deduced for the mass of the neutron. L. L. B.

Loss of velocity of neutrons in heavy water. H. Herszfinkiel, J. Rotblat, and M. Żyw (Nature, 1935, **135**, 653—654).—The radioactivity induced in Ag by neutrons (I) from a Rn+Be source is increased by passing (I) through 98% D_2O, but to a smaller extent than by passage through H_2O. A small increase in the layer of D_2O leads proportionately to an activity > is the case with H_2O, since in the collision of neutrons with diplons the effective scattering probably occurs mainly in a backward direction, whilst with protons it is always in the forward direction. L. S. T.

Disintegration of boron by slow neutrons. B. Kurtschatov, I. Kurtschatov, and G. Latichev (Compt. rend., 1935, **200**, 1199—1201).—B is more readily disintegrated by collision with slow neutrons than with fast neutrons. Such collision leads to the production of two heavy particles, and not three as stated by Chadwick and Goldhaber (this vol., 277), the primary reaction being $_5B^{10}+{}_0n^1 \longrightarrow {}_3Li^7+{}_2He^4$. J. W. S.

Case of artificial radioactivity produced by bombardment with neutrons without capture of the neutron. B. Kurtschatov, I. Kurtschatov, L. Missovski, and L. Roussinov (Compt. rend., 1935, **200**, 1201—1203).—Irradiation of MeBr with neutrons yields γ-ray sources of half-life 18 min., 4—5 hr., and 36 hr. The last product also emits β-rays of about 6×10^5 e.v. It is shown to be an isotope of Br, and it is concluded that it is Br^{78} and that the action of the neutron causes emission of another neutron without fixation of the first. J. W. S.

Radiopotassium and other artificial radio-elements. G. von Hevesy and H. Levi (Nature, 1935, **135**, 580).—K^{42} has been obtained by bombarding $CaCO_3$ by neutrons from a Be+Rn source: $_{20}Ca^{42}+{}_0n^1={}_{19}K^{42}+{}_1H^1$. Owing to the low Ca^{42} content of $CaCO_3$ the yield of K^{42} is small. $_{19}K^{42}$ has thus been prepared from $_{19}K^{41}$, $_{20}Ca^{42}$, and $_{21}Sc^{45}$ by bombardment with $_0n^1$. Neutrons retarded by reflexion by H nuclei yield an active Ca isotope, which decays with a 4-hr. period, due to the reaction $_{20}Ca^{40}+{}_0n^1={}_{20}Ca^{41}$ or, probably, $_{20}Ca^{44}+{}_0n^1={}_{20}Ca^{45}$. Retarded neutrons and Zr give an active Zr decaying with a period of 40 hr., and β-rays. Active Hf, similarly produced, has a half-life period of several months. The reactions are presumably $_{40}Zr^{96}+{}_0n^1={}_{40}Zr^{97}$, and $_{72}Hf^{180}+{}_0n^1={}_{72}Hf^{181}$ and $_{72}Hf^{181}={}_{73}Ta^{181}+\beta$. L. S. T.

Radio-cæsium activated by neutrons. W. M. Latimer, D. E. Hull, and W. F. Libby (J. Amer. Chem. Soc., 1935, **57**, 781—782).—Radio-Cs emits a β-particle. The decay has a half-life period of 80—100 min. E. S. H.

Production of radioactivity by neutrons. J. C. McLennan, L. G. Grimmett, and J. Read (Nature, 1935, **135**, 505).—The radioactivities produced by slow neutrons (cf. this vol., 276) in Zn, $CsNO_3$, TlOAc, and $Bi_2(CO_3)_3$ have half-lives of 100, 75, 97, and 0 min., respectively. The 6-min. half-life for Zn, reported by Fermi, was also obtained. The integral curve method used for calculating these vals. is superior to the differential curve method usually employed. L. S. T.

Artificial radioactivity of iridium. L. Sosnowski (Compt. rend., 1935, **200**, 922—924).—After irradiation with neutrons from Be excited by Ra γ-radiation, Ir shows radioactivity, one product emitting β-rays, half-life 3 days, and the other emitting both β and γ-rays, half-life 50 min. These results are not in accord with those of Fermi *et al.* (A., 1934, 1284). J. W. S.

Artificial transmutation of uranium by neutrons. II. O. Hahn and L. Meitner (Naturwiss., 1935, **23**, 230—231; cf. this vol., 278).—The substances of half-life 13 and 90 min., respectively, formed by the bombardment of U by neutrons, are not

isotopes, but can be separated by chemical methods. The 90-min. substance is a mixture of two elements of half-life 50—70 min. and 2—3 days, respectively, which may be isotopic. All these elements probably have at. no. > 92. A. J. M.

Theory of β-rays and magnetic moment of the proton. G. C. Wick (Atti R. Accad. Lincei, 1935, [vi], **21**, 170—173).—Theoretical. O. J. W.

Position of protons and neutrons in the natural system of elements. C. G. Bedreag (Compt. rend., 1935, **200**, 1197—1199).—A scheme for various nuclei. J. W. S.

Influence of filtration on the properties of the [cosmic] radiation which produces showers [of secondary particles]. B. Rossi and G. Alocco (Atti R. Accad. Lincei, 1935, [vi], **21**, 167—170).—If the cosmic radiation is passed through sufficiently thick layers of matter the frequency of the showers produced is independent of the at. no. of the absorbing element (cf. A., 1933, 996). O. J. W.

Secondary and tertiary particles produced by cosmic rays. J. H. Sawyer, jun. (Physical Rev., 1935, [ii], **47**, 515—521; cf. A., 1933, 996).—The secondaries from Pb have little power to produce detectable tertiaries or showers from Pb or Al. The secondaries from Al produce more showers in Pb than the secondaries from air. A component of the cosmic rays softer than the corpuscular component is probably the chief source of the secondaries producing the showers. N. M. B.

Secondary effect of cosmic rays. M. Ackemann (Z. Physik, 1935, **94**, 303—316).—New max. in secondary ray absorption measurements have been observed. A. B. D. C.

Annihilation of high-energy positive electrons in passing through matter. J. Solomon (J. Phys. Radium, 1935, [vii], **6**, 114—116).—Mathematical. N. M. B.

Theory of the photon. K. V. Nikolski (Compt. rend. Acad. Sci. U.R.S.S., 1935, **1**, 372—377).—Mathematical. W. R. A.

Thermal equilibrium of elementary corpuscles. G. Wataghin (Compt. rend., 1935, **200**, 909—912; cf. A., 1934, 712).—Mathematical. J. W. S.

Synthesis of *X*-ray filtration curves from Kramers' emission law. L. Silberstein (Phil. Mag., 1935, [vii], **19**, 1042—1054; cf. A., 1933, 332).—Theoretical. R. S.

Thomas–Fermi method for metals. J. C. Slater and H. M. Krutter (Physical Rev., 1935, [ii], **47**, 559—568).—Mathematical. N. M. B.

Electromagnetic field of Dirac's electron. K. Nikolsky (Compt. rend., 1935, **200**, 1086—1088).—Dirac's theory is employed to deduce Born and Infeld's system of electro-dynamic non-linear equations (Proc. Roy. Soc., 1934, **A**, **144**, 425). M. S. B.

Electromagnetic mass of the Dirac electron. N. Kemmer (Ann. Physik, 1935, [v], **22**, 674—712).—Theoretical. The usual conception of the electromagnetic mass (I) as the coeff. of the term in the expression for the characteristic force, which ∝ acceleration, is not simply related to that derived from considerations of the self-energy of the electron (A., 1934, 711, 1150). More satisfactory results are obtained from consideration of the theory of "holes." (I) is shown to be ∝ log (electron radius). A. J. M.

Calculation of atom form factors. B. V. S. Nagy (Z. Physik, 1935, **94**, 229—230).—Correction and extension of previous vals. (A., 1934, 1285). A. B. D. C.

Temperature and entropy of light quanta. R. von Hirsch (Ann. Physik, 1935, [v], **22**, 609—628).—Theoretical. The thermodynamic theory of radiation is extended. The thermodynamics (I) of the Compton and photo-effects is discussed. The application of (I) to anomalous dispersion gives results in agreement with experiment. The natural width of spectral lines is calc. A. J. M.

Ideal gases. W. Glaser (Z. Physik, 1935, **94**, 317—328).—Wien's displacement law is applied to particle waves and gives the energy distribution function for a relativistic corpuscular gas. A. B. D. C.

Determination of magnetic moments of molecules by the molecular-ray method. R. Schnurmann (J. Phys. Radium, 1935, [vii], **6**, 99—107).—The Stern–Gerlach method gives satisfactory results for O_2 and NO. N. M. B.

Physical methods in chemistry. II. Absorption spectrum. L. J. N. van der Hulst and P. C. Henriquez (Chem. Weekblad, 1935, **32**, 210—215).—A summary. D. R. D.

Zeeman effect and position of perturbation in the $A^1\Pi$ state of CO. R. Schmid and L. Gerö (Z. Physik, 1935, **94**, 386—396). A. B. D. C.

Band system of neutral OH. III. Identification of the (2′2″), (3′0″), (3′3″), (4′1″), (4′2″), (4′3″), and (4′4″) bands. Formulation of the wave-numbers of the null lines. T. Tanaka and J. Koana (Proc. Phys.-Math. Soc. Japan, 1934, **16**, 365—400).—The spectrum of the O_2–H_2 flame was re-examined. Ch. Abs. (e)

New band system of NH. R. W. Lunt, R. W. B. Pearse, and E. C. W. Smith (Nature, 1935, **135**, 508).—A new band has been observed in the spectrum of a hollow cathode discharge through streaming NH_3. The upper level of the band is identical with that of the 3240 Å. band of the $^1\Pi \longrightarrow {}^1\Delta$ system of NH, and the final level is identified with the lower $^1\Sigma^+$ level predicted for NH. L. S. T.

Spectroscopic constants of the di-atom PN. C. H. D. Clark (Nature, 1935, **135**, 544).—Experimental work (A., 1934, 7) confirms the author's predictions (this vol., 432). L. S. T.

Line absorption spectra of some salts of the transition elements, especially of cobalt and manganese. J. Gielessen (Ann. Physik, 1935, [v], **22**, 537—560).—For Mn salts the absorption spectrum (I) consists of a strong line spectrum (II) and weak, general absorption, generally on the short-wave side of (II). There is a displacement towards the shorter waves, and a contraction of (I) through the series $MnBr_2,4H_2O$, $MnCl_2,4H_2O$, $MnSO_4,H_2O$. (I) of the hydrates of $MnSO_4$ are displaced towards the longer

waves as the no. of mols. of H_2O decreases. The chief absorption range is the same for all Mn salts investigated, both solid and in solution. For $NiCl_2,6H_2O$ and $NiBr_2,6H_2O$ at −189° there are two strong absorption bands, between which there are alternate strong and weak bands. $CuCl_2,2H_2O$, $CuSO_4,5H_2O$, and various salts of Mo and W showed no selective absorption. (I) was investigated for many Co salts, and mixtures of Co halides with alkali halides and $ZnCl_2$. (I) of these salts shows a line absorption, a weak general absorption, and for $CoCl_2,6H_2O$ and $CoBr_2,6H_2O$ a strong continuous absorption, which for thin crystals may be split into a doublet. The effect on (I) of dehydration is the same as for Mn salts. Mixing $CoCl_2$ with the isomorphous $ZnCl_2$ produces displacement, as well as a new (I). Mixtures of $CoCl_2$ and alkali halides have entirely new (I). A. J. M.

Absorption spectra of chlorides and oxychlorides of sulphur in the vapour state. R. K. Asundi and R. Samuel (Current Sci., 1935, **3**, 417—418).—In the vapour state SCl_2, S_2Cl_2, and $SOCl_2$ show a strong absorption band in the region 2400—2900 Å., having its origin in $p-p$ linking between S and Cl. The absorption spectrum of SCl_2 is analogous to that of OCl_2. W. R. A.

Critical investigation of the absorption spectrum of potassium nitrate in the ultra-violet by the spectrographic and photo-electric method. J. Eeckhout (Natuurwetensch. Tijds., 1935, **17**, 72—80).—A simple photo-electric method for measuring absorption in the ultra-violet is described, and applied to solutions of KNO_3, which shows max. absorption from λ 2970 to 3050. The error is reduced to 2%. S. C.

Absorption spectra of substances containing alkyl radicals. H. W. Thompson and J. J. Frewing (Nature, 1935, **135**, 507—508).—Results obtained with the ultra-violet absorption spectra of $HgEt_2$, $GeMe_4$, NEt_3, Me_2O, Et_2O, PEt_3, and Et_2S are outlined. L. S. T.

Absorption spectra of polycyclic hydrocarbons. I. Alkyl-substituted phenanthrenes. II. Partly reduced derivatives of phenanthrene etc. F. A. Askew (J.C.S., 1935, 509—512, 512—516).—I. Ultra-violet absorption spectra of 18 alkyl-substituted phenanthrenes are described, and their relationships to the *cyclo*-compounds are discussed.

II. Relationships between the spectra of 9 : 10-dihydro-, tetrahydro-, and two isomeric octahydrophenanthrenes, *cis*- and *trans*-hexahydrochrysene, 7 : 8-dihydrophenalyl-7-*spirocyclo*pentane, and fluorene, and those described above are discussed. It is shown that previous results for fluorene have been obtained with impure material. F. L. U.

Ultra-violet absorption spectra of derivatives of diphenylene sulphide and of diphenylene sulphone. M. Chaix (Compt. rend., 1935, **200**, 1208—1210; cf. A., 1933, 1227).—Data have been obtained for 2 : 7- and 3 : 6-dichloro- and -dibromo-diphenylene sulphone and for 2- and 3-chloro-diphenylene sulphone, in EtOH solution. 3- or 3 : 6-substituents decrease the sharpness of the diphenylene sulphone bands at 3250, 2900, and 2820 Å., whilst the 2430 Å. band remains sharp, but is shifted to longer λ. The absorption bands of 2- and 2 : 7-compounds are all sharp, but are shifted 50—100 Å. towards longer λ. 2 : 7-Compounds are more highly coloured than 3 : 6-compounds. Br exerts more bathochromic effect than Cl. J. W. S.

Relations between the optical properties of the medium and the photochemical constants of tetraphenylrubene. Absorption spectrum. C. Dufraisse and M. Badoche (Compt. rend., 1935, **200**, 929—931).—Solutions of 1 : 1′ : 3 : 3′-tetraphenylrubene (I) in C_6H_6 obey Beer's law. The absorption max. of solutions of (I) in 16 different org. solvents are not identical, but the absorption curve is of const. form. With one exception the order of the displacement follows Kundt's rule. The displacements are not due to mol. association with the solvent. J. W. S.

Continuous absorption spectra of polyatomic molecules. V. Y. Hukumoto (Sci. Rep. Tôhoku, 1935, **23**, 846—851; cf. A., 1933, 661).—Absorption-limit data are tabulated for 18 alcohols, MeOH—$C_{12}H_{25}$·OH. Dissociation energies of linkings are given and are discussed in relation to mol. structure. N. M. B.

Influence of temperature on the absorption of some organic liquids in the near infra-red. B. Bloch and M. Errera (J. Phys. Radium, 1935, [vii], **6**, 154—158).—A detailed account of work already noted (A., 1934, 1288).

Infra-red spectrum, normal frequencies, and intramolecular forces in selenium and tellurium hexafluorides. H. Sachsse and E. Bartholomé (Z. physikal. Chem., 1935, **B**, **28**, 257—266).—From measurements of the infra-red spectra at 3—25 μ and the sp. heats, the normal frequencies have been determined, and from them by means of the general force law the seven general force consts. calc. As for SF_6 (A., 1934, 1055) the principal consts. can be represented by a system of Coulomb forces, but others, especially those involved in the interaction of neighbouring atoms, are considerably affected by angular forces. R. C.

Intermolecular isomerism of α-picoline studied in the far infra-red. C. H. Cartwright and J. Errera (Compt. rend., 1935, **200**, 914—916).—Measurements of the refractive index of α- (I) and β-picoline between 52 and 152 μ indicate that the at. polarisation is about 0·1 cm.^{3} in each case, and not 23·2 cm.^{3} as found by Rau *et al.* (A., 1934, 943) for (I). The existence of a tautomeric form of (I) is therefore not confirmed by the results. J. W. S.

Intensity of Raman lines as a function of the frequency of the incident rays. L. S. Ornstein and J. J. Went (Physica, 1935, **2**, 391—398).—The relationship between the intensity of Raman radiation and the frequency of the incident light was determined for crystals of calcite (I) and quartz (II). For (II) the ratio of intensities of Raman to incident radiation is equal to $(\nu-\nu_r)^4$, where ν, ν_r are the frequencies of the incident and Raman light, respectively. For (I) this does not hold owing to ultra-violet absorption. The reason for this is discussed. A. J. M.

Raman spectrum of deuterium. T. F. Anderson and D. M. Yost (J. Chem. Physics, 1935, **3**, 242—243).—Raman spectra of gaseous D_2 (99·5% purity) have been obtained at a pressure of 2·5 atm. The frequencies are in agreement with those calc. from Urey and Teal's equation (Rev. Mod. Physics, 1935, **7**, 34). The result is important in connexion with the use of D to establish the structure of mols. containing H, since it indicates that the D—D distance is the same as the H—H distance, and, therefore, the M—D and M—H distances, where M is any atom, may be assumed equal. The force const. for D is also the same as for H. M. S. B.

Raman spectra of fused salts. E. J. Salstrom and L. Harris (J. Chem. Physics, 1935, **3**, 241—242).—Raman spectra have been observed for fused $ZnCl_2$ and $ZnBr_2$. The fact that these persist at about 100° above the m.p. indicates that the frequencies are not due to vibrations in the crystal lattice, but probably to oscillations in the Zn halide grouping. The mol. is not linear. No Raman lines have been observed for fused LiBr, $PbCl_2$, $PbBr_2$, and $CdCl_2$, but the experimental conditions were less satisfactory for these than for the Zn salts. M. S. B.

Magnetic and Raman spectra evidence on the structure of complex cyanides. D. M. Bose (Indian J. Physics, 1935, **9**, 277—286).—The Raman spectra of the double K cyanides of Ag, Ni, Zn, Cd, Cu, Co, Rh, Cr, Fe, and Ru can be interpreted on the assumption that the CN groups are present as double mols. $(CN)_2$, linked to the central paramagnetic atom by single or double linkings as indicated by magnetic properties. N. M. B.

Raman effects of organic molecules. (Vibration structure of acetylenes.) B. Timm and R. Mecke (Z. Physik, 1935, **94**, 1—10).—Vibrational frequencies are given for $(\cdot C{:}CH)_2$ and $CH_2{:}CH\cdot C{:}CH$, and are assigned to the different groups. A. B. D. C.

Raman effect. XLI. Transition from vibrational spectra of XY_4 to those of XZ_4. K. W. F. Kohlrausch (Z. physikal. Chem., 1935, **B**, **28**, 340—350).—The transition of vibrational forms in $XY_4 \longrightarrow ZXY_3 \longrightarrow Z_2XY_2 \longrightarrow Z_3XY \longrightarrow Z_4X$ is worked out theoretically and the results are applied to the data for $CCl_4 \longrightarrow CMe_4$, $CCl_4 \longrightarrow CH_4$, and $CBr_4 \longrightarrow CH_4$. R. C.

Raman spectra of methyldiethylcarbinol, benzyldimethylcarbinol, and the corresponding ethylenic hydrocarbons. J. Savard (Bull. Soc. chim., 1935, [v], **2**, 633—640).—The data are compared with those for $CMe_2Et\cdot OH$ (Nevgi *et al.*, A., 1934, 1056). D. R. D.

Rotational Raman scattering in benzene vapour. S. C. Sirkar (Indian J. Physics, 1935, **9**, 295—298).—A detailed account of results previously reported (cf. this vol., 146). N. M. B.

Raman spectra of dimethyl and diethyl trisulphides. N. G. Pai (Indian J. Physics, 1935, **9**, 231—238).—Raman data are tabulated, and show that the compounds are not solutions of S in the corresponding disulphides, and that they do not contain a double linking. The probable structure is $S(SR)_2$. N. M. B.

Raman spectra of organo-metallic compounds. N. G. Pai (Proc. Roy. Soc., 1935, **A**, **149**, 29—35).—The Raman spectra of $ZnMe_2$, $ZnEt_2$, $HgMe_2$, $HgEt_2$, $BiMe_3$, $SnMe_4$, and $PbEt_4$ have been studied. Some of the lines show exceptionally large intensities. The dialkyls may be treated as symmetrical non-linear triatomic mols. of the type XY_2, in which X has a large valency angle. $BiMe_3$ conforms to a pyramidal model, whilst the tetra-alkyls have a regular tetrahedral structure. L. L. B.

Absorption and fluorescence of the vapours of cuprous halides. J. Terrien (Compt. rend., 1935, **200**, 1096—1098).—Ultra-violet radiations of $\lambda < 2400$ Å. excite a bluish-green to blue fluorescence in Cu_2Cl_2 or Cu_2Br_2 vapour as the pressure rises. The intensity of emission $\propto$ the first power of the exciting intensity, indicating the absorption of a single quantum of short λ. The energy thus acquired by 1 mol. of Cu_2Cl_2 is not sufficient to dissociate it into 2CuCl and excite one of the mols. M. S. B.

Quenching of fluorescence of liquids by halogen ions. E. Schneider (Z. physikal. Chem., 1935, **B**, **28**, 311—322).—The quenching of fluorescence is related to the photo-oxidation of iodide solutions sensitised by fluorescent substances. In the latter the quantum yield of I formation, referred to the no. of quanta absorbed by the fluorescent substance, ≈ 1. Extinction probably depends on $I' + H_2O + Q = HI + OH'$, where Q is the amount of energy which would appear as the quantum of fluorescence radiation in absence of a collision of the second kind. It seems that in the photo-oxidation each HI mol. reacts with O before ionisation, an I_2 mol. being formed from each two HI mols. R. C.

Fluorescence spectrum of apatite in ultra-violet light. E. Iwase (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, **27**, 1—9).—Fluorescent apatites (I) from Japan, Canada, Germany, and Norway have been examined. (I) occurring in ore veins in tabular crystals give two broad bands in the orange-yellow and blue-violet regions, whilst in the case of prismatic (I) in basic igneous rocks, the bands are less intense. The difference in crystal habit and fluorescence spectrum is attributed to the presence of impurities. R. S.

Thermal rotations of fluorescent molecules and duration of luminescence. A. Jabłoński and W. Szymanowski (Nature, 1935, **135**, 582).—Contrary to theoretical expectations, the duration of luminescence of fluorescein in H_2O or EtOH is $>$ in glycerol. The effect of thermal rotations of the dye mols. can account for this anomalous behaviour. L. S. T.

Mechanism of activation of oxygen by fluorescent dyes. J. Franck and H. Levi (Naturwiss., 1935, **23**, 229—230).—The photo-sensitised oxidation of *iso*amylamine in the presence of chlorophyll (I) is considered. The theory of Krautsky (this vol., 311), postulating the existence of metastable conditions of excitation, is criticised. If the O_2 derives all its energy from the metastable condition, in order that the quantum efficiency may approach unity (Gaffron, A., 1933, 1214), the fluorescence should be extinguished by O_2

at relatively small concns.; this does not occur. It is suggested that the observed phosphorescence of (I) is a chemiluminescence. The absorption of light by (I) results in the removal of loosely-bound H atoms from (I) and formation of a radical in solution. The recombination energy may re-excite (I) giving rise to chemiluminescence. If O_2 is present, it combines with the liberated H, and after a period of exposure all the available H of (I) is used up, the acceptor then using the energy of (I), being thus rendered capable of reacting with O_2. A. J. M.

Photoluminescence of dye phosphors. A. JABŁOŃSKI (Z. Physik, 1935, **94**, 38—46).—Mols. capable of phosphorescence have at least one metastable level: the case of one level is investigated and accounts for temp. variation of phosphorescence. A. B. D. C.

Internal recombination during photo-dissociation of polyatomic molecules. A. TERENIN (Nature, 1935, **135**, 543—544).—The photo-decomp. of SnI_4 vapour by light of 2500—2150 Å. is accompanied by a bright visible emission of the spectrum of I_2 with an abnormal distribution of intensity in the bands. The I_2 mol. is detached from the SnI_4 mol. in one primary process. The whole process is equiv. to a recombination of atoms in the act of photo-dissociation, or to a redistribution of valency linkings. A marked temp. coeff. indicates the necessity for an energy of activation for this type of photo-dissociation. The mechanism of the yellow fluorescence in BiI_3 vapour is similarly explained; under the action of suitable quanta and with some thermal activation an I mol. is detached from BiI_3. L. S. T.

Ionisation in gases by *X*-rays. L. H. MARTIN, J. C. BOWER, and T. H. LABY (J. Cancer Res. Comm. Sydney, 1935, **6**, 131—143).—Cloud expansion chamber experiments are described and their bearing on the measurement of *X*-ray intensities by ionisation methods is discussed. E. A. H. R.

Photo-dissociation of single crystals of potassium and sodium nitrates under polarised light. K. S. KRISHNAN and L. K. NARAYANASWAMY (Current Sci., 1935, **3**, 417).—Nitrates of NH_4, Na, K, Sr, Ba, Cd, Al, and Pb are dissociated to nitrites by light of $\lambda < 250$ mμ. The dissociation appears to be confined to a surface layer 20 μ thick. Under linearly polarised light single crystals of NH_4NO_3, $NaNO_3$, and KNO_3 show greater dissociation when the electric vector of the exciting light is in the plane of the NO_3' ions than when it is along the normal to the NO_3' ion plane. $KClO_3$ crystals show similar anisotropic photo-dissociation. W. R. A.

Photo-electric study of monocrystalline sulphur. A. A. VOROBIEV (J. Exp. Theor. Phys. U.S.S.R., 1934, **4**, 368—383).—On illumination (even with infra-red rays) S crystals become semiconductors. The effect persists for several min. after removing the light source. CH. ABS. (*e*)

Rectification of alternating current by crystals. S. R. KHASTGIR and A. K. D. GUPTA (Indian J. Physics, 1935, **9**, 255—276).—Two types of rectification were established; one type, in symmetrical crystals (galena, Fe pyrites, magnetite, molybdenite, pyrolusite, cassiterite, and bornite), is associated with point contacts; the other type, a vol. rectification due to asymmetric conductance, is found for crystals having no centres of symmetry (carborundum, zincite, and Si). N. M. B.

Red threshold of inner photo-effect and emission work for semi-conductors. J. H. DE BOER and W. C. VAN GEEL (Physica, 1935, **2**, 286—298).—The thermal emission work, U, obtained from the effect of temp. on the conduction of a semi-conductor (I), is not equal to the energy val. $h\nu_r$ of the red threshold of the photo-electric conduction of (I). The Wilson theory of (I) (Proc. Roy. Soc., 1931, **A**, **133**, 458) gives $2U=h\nu_r$, which also does not hold. The theory is criticised. A theory of (I) is put forward, supposing that semi-conduction consists of an ionisation of internally adsorbed atoms, which involves alterations in the binding energies. Potential curves are drawn for the various possible cases, and it is shown that $h\nu_r \neq U$. A. J. M.

Asymmetric conductivity of an electrode system: metal–salt–adsorbed alkali metal. J. H. DE BOER and W. C. VAN GEEL (Physica, 1935, **2**, 309—320).—A cell with a thin electrode ($\not> 2$ μ) composed of Ag–CaF_2–Cs shows asymmetric conductivity. This effect must be ascribed to differences in surface structure of the two metal electrodes. The Cs electrode (I), being adsorbed in holes in the salt layer, behaves like a set of points, thus producing an intense field, making the electron emission of (I) > that of the Ag. A. J. M.

Asymmetric conductivity of the combination: metal–insulating layer–salt layer–adsorbed alkali metal. W. C. VAN GEEL and J. H. DE BOER (Physica, 1935, **2**, 321—327).—A cell of the type Ag–shellac layer–CaF_2–K shows asymmetric conductivity. With alkali metal (I) positive, the relationship between current (i) and potential (V) is $i=Ae^{-B/V}$; with (I) negative, $i=CV^{3/2}$. The phenomenon depends on electron emission in the cold. The insulating layer prevents conducting bridges through the salt layer. A. J. M.

Photo-electric fatigue and oxidation. J. S. HUNTER (Phil. Mag., 1935, [vii], **19**, 958—964; cf. A., 1934, 1149).—Photo-electric spectral distribution curves have been determined for Ag_2O, Bi_2O_3, and Ni_2O_3. Comparison of photo-electric thresholds indicates that an oxide film is not immediately formed when a clean metal surface is exposed to the air, but that adsorption occurs. R. S.

Action of gases (H_2, N_2, O_2) on dye photo-cells. (MLLE.) C. STORA (Compt. rend., 1935, **200**, 1191—1194; cf. A., 1934, 717; this vol., 586).—The negative photo-potential observed with certain dyes on metal electrodes in aq. K_2SO_4 in presence of O_2 is reversed in N_2 and may become strongly positive on passing H_2 through the solution. The negative photo-potential is attributed to the buffering effect of the atm. O_2, eliminating any effect of the O_2 produced by photolysis of the H_2O, this being eliminated on passage of H_2. J. W. S.

Ionic rays. A. MENTRUP (Physikal. Z., 1935, **36**, 335—340).—The conditions for producing ionic rays

strong enough for investigation in the mass spectrograph were studied with CdI_2, $PbCl_2$, TlCl, AgBr, and LiCl. By increasing the surface bearing the salt, it is easy to obtain a current of 10^{-7} amp. at comparatively low temp. No saturation was obtained up to a potential of 90 volts, except in the case of LiCl (30 volts). A. J. M.

Electrical conductivity of compressed graphite powder. Z. Specht (Z. Elektrochem., 1935, **41**, 204—206; cf. A., 1933, 114).—A reply to criticisms by Brunner and Hammerschmid (A., 1934, 367). F. L. U.

[Electrical conductivity of compressed graphite powder.] J. Brunner and H. Hammerschmid (Z. Elektrochem., 1935, **41**, 206—207).—A rejoinder to Specht (preceding abstract). F. L. U.

Determination of the resistance of carborundum by the eddy-current effect. L. I. Rusinov (J. Tech. Phys. U.S.S.R., 1934, **4**, 319—327).—The sp. resistance was 0·5. There was no indication of highly conducting particles between the SiC grains. Ch. Abs. (*e*)

Insulating powers of amber, quartz glass, and sulphur in dry and moist air. W. Gnann (Physikal. Z., 1935, **36**, 222—230).—The resistance and polarisation currents were determined. A. J. M.

Electrical conductivity of homopolar compounds. A. M. Zolotareva (J. Exp. Theor. Phys. U.S.S.R., 1934, **4**, 384—387).—For $C_{10}H_8$ monocrystals the initial sp. conductivity (I) at 18° is $< 3\times10^{-11}$, and the residual (I) at 52° $< 10^{-18}$ mho. Ch. Abs. (*e*)

Influence of photo-electric current on the breakdown voltage. B. M. Vul and I. M. Goldman (Compt. rend. Acad. Sci. U.R.S.S., 1935, **1**, 363—365).—The breakdown voltage of 20 coloured NaCl crystals has been examined under the influence of d.c., a.c., and suddenly impressed voltage. One half of the crystal was illuminated, the other half darkened. With suddenly impressed voltages no differences were observed between the two halves of the crystal. W. R. A.

Breakdown and conductivity in thin layers of liquids. T. Meyer (J. Chim. phys., 1935, **32**, 199—209).—Conductivity and temp. coeffs. are given for 18 org. liquids under standard conditions < breakdown (applied p.d.=350 volts across 20 μ). In poorly conducting media, current after breakdown ∝ voltage, but the effective resistance is independent of the thickness of the film. D. R. D.

Rotations of molecules in solids and of the dielectric constant of solids and liquids. R. H. Fowler (Proc. Roy. Soc., 1935, **A, 149**, 1—28).—Mathematical. Calculations are made of the changes of sp. heat and energy content in a transition region of a solid, and of the dielectric const. of a polar liquid and of Na K tartrate, which are in fair agreement with the experimental data. L. L. B.

Dielectric constant of liquids under high pressure. Z. T. Chang (Chinese J. Physics, 1934, **1**, 1—55).—ϵ for PhMe, CS_2, *n*-C_5H_{12}, *n*-C_6H_{14}, and Et_2O has been determined at 30° and 75°, and for *iso*-C_5H_{11}·OH at 22·4°, at pressures 1—12,000 kg. per sq. cm., and at frequencies 600, 1000, and 2000 cycles per sec. ϵ is almost independent of frequency except for Et_2O and C_5H_{11}·OH. $(\epsilon-1)/\{(\epsilon+2)d\}$ decreases with increasing pressure, the decrease increasing with the electric moment. R. S. B.

Measurement of absorption of short electric waves in dipole liquids. J. Malsch and E. Keutner (Physikal. Z., 1935, **36**, 288—292).—The method of Haase and Krause (A., 1934, 240, 1057) was used with C_5H_{11}·OH, BuOH, PrOH, and EtOH. The absorbed energy is independent of λ, in agreement with dipole theory, but contrary to the results of Haase and Krause. The method is suitable for determining the const. *y*, governing the relaxation time in Debye's equation. The vals. of *y* for the above alcohols and hexyl alcohol are given. A. J. M.

Dielectric properties of acetylenic compounds. V. Acetylenic halides and alcohols. J. A. Toussaint and H. H. Wenzke (J. Amer. Chem. Soc., 1935, **57**, 668—670; cf. A., 1934, 1292).—The moments of the acetylenic halides are influenced by the position of the triple linking, greatest with I- and least with Cl-compounds. The moments of the acetylenic alcohols are > those of the *n*-aliphatic alcohols. The moments of α-hydroxy-Δ^2- and -Δ^3-octinene, -Δ^3-noninene, -Δ^2-heptinene, α-chloro-, α-bromo-, and α-iodo-Δ^2-heptinene and -octinene, and α-hydroxy-*n*-heptane have been determined. E. J. S.

Effect of the hydrogen linking on the dielectric constants and b.p. of organic liquids. W. D. Kumler (J. Amer. Chem. Soc., 1935, **57**, 600—605).—By eliminating or making const. the effects of temp., electronic polarisation, at. polarisation, and no. of mols. per c.c., the relation between interaction of the mols. and dielectric const., ϵ, has been studied. Liquids that do not form H linkings have normal ϵ and *vice versa*. The conditions for the formation of H linkings are formulated. The structures of the association complexes in the liquid state of the carboxylic acids, HF, and HCN are discussed. H linkings raise the b.p. of the liquids considered by an average of 76°. The mol. wts. of NH_2Ac, NHEtAc, and NEt_2Ac in C_6H_6 have been determined. The connexion between H linking formation and resonance in amides is discussed. E. S. H.

Electric moments of dialkoxyalkanes. M. M. Otto (J. Amer. Chem. Soc., 1935, **57**, 693—695).—The electric moments of ββ-dimethoxy-, -diethoxy-, and -dipropoxy-heptane, $CH_2(OEt)_2$, and $CH_2(O{\cdot}CH_2Bu^\gamma)_2$ have been determined. Evidence for the constancy of the valency angle $>C<^{O\cdot}_{O\cdot}$, where the two other attached groups are two H and that containing an amyl and a Me, is adduced. E. S. H.

Dipole moments of associated liquids. F. R. Goss (J.C.S., 1935, 502—506; cf. A., 1934, 717).—Differences between the dielectric polarisation of liquids and gases are attributed mainly to decreases due to anisotropy and association of the solvent, and to an increase due to association of the solute. A formula for the polarisation of liquids is deduced

and exemplified by reference to $PhNO_2$ in various solvents. F. L. U.

Dipole moments of *p*-cymene, 2- and 3-halogeno-*p*-cymenes, carvacrol, thymol, *p*-ethyltoluene, *p-tert.*-butyltoluene, 1 : 3-dimethyl-5-*tert.*-butylbenzene, *tert.*-butylbenzene and its *p*-nitro-derivative. C. G. Le Fèvre, R. J. W. Le Fèvre, and (in part) K. W. Robertson (J.C.S., 1935, 480—488; cf. A., 1933, 1153).—Dipole moments of the substances named have been determined, and are discussed with reference to the influence of the various substituents. F. L. U.

Electric moments of monohydric normal, secondary, and *iso*-alcohols. P. C. Mahanti (Z. Physik, 1935, **94**, 220—223).—Dipole moments of monohydric *sec.*- and *iso*-alcohols of the aliphatic series are of the same order as those of primary alcohols, indicating that the moments are independent of the position of the OH, and of the branching of C chains. A. B. D. C.

Electric moment of some derivatives of the heterocyclic ring C_2N_2O. M. Milone (Gazzetta, 1935, **65**, 152—158).—The dipole moments of certain furazans, azoximes, and oxdiazoles have been measured. The vals. of μ for the three classes of compound are 4·0—4·7, 1·4—1·65, and $3·3—3·9\times10^{-18}$ e.s.u., respectively. The val. of μ can be used for identifying the isomeric derivatives of the three C_2N_2O ring structures. O. J. W.

Dioximes. CVII. M. Milone (Gazzetta, 1935, **65**, 94—102).—The magnetic moments of glyoxime, and its Me, Me_2, Me Et, Me Pr^a, Me C_8H_{17}, Ph (α and β), *p*-C_6H_4Me (α and β), Ph Me (α and β), and Ph_2 (α, β, and γ) derivatives, in dioxan solution are respectively 1·22, 0·882, 1·38, 1·106, 1·25, 1·485, 1·396, 1·702, 1·089, 1·66, 0·782, 1·161, 1·492, 2·12, and 1·55, each $\times 10^{-18}$. The β-forms, having the greater moment, presumably have the *amphi*-configuration (cf. A., 1931, 1156). E. W. W.

Directive influence of the electric moment on substitution in the benzene ring. W. J. Svirbely and J. C. Warner (J. Amer. Chem. Soc., 1935, **57**, 655—657).—If a mono-substituted C_6H_6 derivative possesses an electric moment $> 2·07D$, a second group will be directed to the *m*-position; if the moment is $< 2·07D$, the second group will be directed to the *o*- and *p*-positions. The principle of former polarity rules is not violated. E. S. H.

Detection of molecular interactions by the time of relaxation of polar molecules. P. Girard and P. Abadie (Compt. rend., 1935, **200**, 1187—1189).—The dispersions of pure alcohols and their mixtures with C_6H_6 have been studied and the times of relaxation (τ) of the mols. under various conditions deduced. τ increases initially on dilution, and reaches a max. in about 40—50% solutions, after which it diminishes. It is concluded that two types of mol. interaction can occur concurrently, and that these increase and diminish the time of relaxation, respectively. J. W. S.

Molecular volume of carbamide in complex ions. H. Nakagawa (Bull. Chem. Soc. Japan, 1935, **10**, 130—134).—The mol. vol. of $CO(NH_2)_2$ (R) has been determined in the following complex salts: $[CaR_6]Br_2$, $[CaR_6]I_2$, $[CrR_6]Cl_3,3H_2O$, $[FeR_6]Cl_3,3H_2O$, $[AlR_6]I_3$, $[AlR_6](ClO_4)_3$. The average val. approximates closely to the theoretical. Where H_2O of crystallisation was present its calc. mol. vol. was normal. M. S. B.

Refraction and dispersion of crystals. XI. Rotating prism method of determining dispersion photographically. P. Wulff and T. F. Anderson (Z. Physik, 1935, **94**, 28—37; cf. A., 1934, 718).—A prism rotated continuously gives an edge on a photographic plate corresponding with min. deviation, and so gives the dispersion of the medium. Refractive indices for CsCl between 2000 and 7000 Å. are given to the fourth place. A. B. D. C.

(A) Anomalous dispersion in potassium vapour at high temperatures. V. K. Prokofiev. **(B) Anomalous dispersion near the first two doublets of the principal series of rubidium and cæsium.** V. K. Prokofiev and G. Shtandel (J. Exp. Theor. Phys. U.S.S.R., 1934, **4**, 347—358, 359—367).—(A) Vals. of $n-1$ at 4000 Å. for KI and KBr vapours are 10^{-4} and 5×10^{-5}, respectively.

(B) Measurements with Rb and Cs vapours are recorded. Ch. Abs. (*e*)

Optical constants of the alkali metals. M. I. Sergeev and M. G. Chernikhovski (J. Exp. Theor. Phys. U.S.S.R., 1934, **4**, 235—241).—Formulæ are given for the absorption and dispersion of light by alkali metals and compared with data for K and Na. Ch. Abs. (*e*)

Optical properties of salts in the system $(NH_4)_2SO_4$–$CaSO_4$–H_2O. A. Gabriel (J. Amer. Chem. Soc., 1935, **57**, 686—688).—The following vals. are recorded: $(NH_4)_2SO_4,5CaSO_4,H_2O$, n_α 1·567, n_β 1·580, n_γ 1·595; $(NH_4)_2SO_4,2CaSO_4,H_2O$, n 1·532; $(NH_4)_2SO_4,CaSO_4,H_2O$, n_α 1·521, n_β 1·529, n_γ 1·531. E. S. H.

Pasteur's principle of molecular dissymmetry: *dextro*- and *lævo*-camphoric acids. B. K. Singh (Current Sci., 1935, **3**, 420—421).—Campbell's measurements (A., 1931, 848) on the rotatory power of *d*- and *l*-camphoric acids are repeated. Results are given for 10 λλ between 4358 and 6709 Å. Contrary to Campbell no difference is found in [α] for the two enantiomorphs in EtOH. W. R. A.

Optical rotatory dispersion of α- and β-pinenes in the ultra-violet. R. Padmanabhan and S. K. K. Jatkar (Current Sci., 1935, **3**, 419—420).—β-Pinene gives no max. on the positive side of its rotatory dispersion curve. Neither α- nor β-pinene in EtOH gives max. at 2800 Å. as reported by Servant (A., 1932, 215). W. R. A.

Anomalous magnetic rotation of uranyl nitrate. P. L. Kapur and M. R. Verma (Current Sci., 1935, **3**, 419).—The mol. magnetic rotation, 5·2, is const. over a wide range of concn. Unlike that of most diamagnetic substances, the Faraday effect is negative. W. R. A.

Planar configuration for quadricovalent nickel, palladium, and platinum. E. G. Cox, F. W. Pinkard, W. Wardlaw, and K. C. Webster (J.C.S.,

1935, 459—462).—Salicylaldoxime reacts with aq. K_2PtCl_4 to give a mixture of *disalicylaldoximinoplatinous chloride* and *disalicylaldoximeplatinum* (I). (I) occurs in two modifications, neither of which is isomorphous with the corresponding Pd (II) or Ni (III) compound. *X*-Ray examination has shown (II) and (III) and one of the modifications of (I) to have a planar *trans*-configuration. (III) is diamagnetic. Pauling's theoretical conclusions (cf. A., 1931, 670) are thus substantiated. F. L. U.

Valency defined. E. A. Flood (J. Chem. Educ., 1935, **12**, 132—134).—A discussion. L. S. T.

Inner-complex salts. S. A. Vosnessenski (Uspekhi Khim. U.S.S.R., 1934, **4**, 531—562).—A review. Ch. Abs. (*r*)

New models of old molecules. T. H. Hazlehurst, jun., and H. A. Neville (J. Chem. Educ., 1935, **12**, 128—132).—The construction and uses of mol. models which illustrate recent knowledge of at. structure are described. L. S. T.

Normal vibration frequencies of NH_3, PH_3, and AsH_3. J. B. Howard (J. Chem. Physics, 1935, **3**, 207—211).—Assuming the existence of valency forces in NH_3, PH_3, and AsH_3, it can be shown that the high-frequency degenerate normal vibration, although theoretically active, does not appear as a fundamental in the infra-red spectra. The remaining three observed fundamentals can be accounted for satisfactorily. Fundamental frequencies have also been calc. for the isotopic mols. NH_2D, NHD_2, and ND_3, and provide a test for the val. predicted for the fourth fundamental in NH_3. M. S. B.

Calculation of the fundamental frequencies of a molecule of the type X_6 with plane hexagonal symmetry. M. C. Manneback (Ann. Soc. Sci. Bruxelles, 1935, **55**, B, 5—15; cf. this vol., 150).—The potential energy function and the frequencies of the fundamental modes of vibration are considered. R. S.

Rotating axes and polyatomic molecules. C. Eckart (Physical Rev., 1935, [ii], **47**, 552—558; cf. A., 1934, 1164).—Mathematical. N. M. B.

Dipole rotation in solid non-crystalline materials. A. Gemant (Phil. Mag., 1935, [vii], **19**, 746—758).—Theoretical. The application of Debye's theory of dipole rotation to amorphous solids such as paraffin, glass, etc. is justified. F. L. U.

Interrelation of equilibrium nuclear distance with other molecular constants for diatomic molecules. R. A. Newing (Phil. Mag., 1935, [vii], **19**, 759—767).—A preliminary theoretical investigation of the general properties of potential curves for diat. mols. F. L. U.

Electrostatic energies of ionic lattices. F. Hund (Z. Physik, 1935, **94**, 11—21).—Energies are calc. for lattices of the types AB and AB_2; apart from the no. and charges of the ions, the co-ordination nos. determine the energies of the lattice. A. B. D. C.

Resolution of bond eigenfunctions in terms of a linearly independent set. H. Eyring and H. Gershinowitz (J. Chem. Physics, 1935, **3**, 224—229).—A method for obtaining coeffs. in the expansion of a bond eigenfunction in terms of a linearly independent set has been devised. Coeffs. of eigenfunctions, expanded in terms of the Rumer set, may be determined for 6 linkings. M. S. B.

Quantum-mechanical treatment of molecules by the method of spin valency. G. Wheland (J. Chem. Physics, 1935, **3**, 230—240).—Mathematical. A consideration of the Slater method compared with that of Born, Heitler, Reimer, and Weyl. M. S. B.

General relation between vibration frequencies of isotopic molecules. Calculation of harmonic force constants. O. Redlich (Z. physikal. Chem., 1935, **B**, **28**, 371—382).—Theoretical. The frequencies of a particular type of vibration in two isotopic mols. are connected by an equation which involves only at. masses and moments of inertia, and not force consts. Comparison of the results deduced from this equation with experimental data for $CDCl_3$ (this vol., 146) shows slight discrepancies probably due to anharmonicity of the vibrations. R. C.

Internuclear distance and vibration frequency in diatomic molecules. H. S. Allen and A. K. Longair (Phil. Mag., 1935, [vii], **19**, 1032—1041).—Formulæ connecting internuclear distance r_e and vibration frequency ω_e of diat. mols. are discussed and a new relation $\omega_e r_e^3 \sqrt{\mu} = \text{const.}$, where μ is the reduced mass in g., is proposed. The val. of the const. $\propto$ the no. of completed electronic shells in the mol. R. S.

Ratio of the temperature coefficients of surface tension and density. L. Sibaiya (Current Sci., 1935, **3**, 418—419).—Theoretical. The experimental law that temp. coeff. (of surface tension)/coeff. of expansion has vals. between 2 and 3 is derived from Laplace's theory of capillarity. W. R. A.

Directional distribution of characteristic *X*-rays emitted within crystals. W. Kossel, V. Loeck, and H. Voges (Z. Physik, 1935, **94**, 139—144).—Characteristic radiation of at. groups within a crystal is excited when the crystal forms an anticathode; its directional distribution due to Bragg reflexions has been studied for a single Cu crystal. A. B. D. C.

Precision measurements by the Debye–Scherrer method. M. Straumanis and O. Mellis (Z. Physik, 1935, **94**, 184—191). A. B. D. C.

***X*-Rays from a Lenard tube with a platinum attachment.** F. Schmidt (Physikal. Z., 1935, **36**, 283—288).—A review of the history of the discovery of *X*-rays shows that Röntgen used a Lenard tube, and not a Hittorf or Crookes tube. Experiments with a replica of his apparatus show that the *X*-rays from it are strong, and easily detected by means of a Ba platinocyanide screen as used by Röntgen. The rays were not discovered by Lenard, although working with a similar tube, owing to his lack of detecting apparatus. A. J. M.

Scattering of *X*-rays at small angles. J. A. Gray (Canad. J. Res., 1935, **12**, 408—409; cf. A., 1930, 833).—Powders show either intense scattering at small angles, similar to that of gases (shown by artificial graphite, charcoal, and Si), or scattering due to refraction in or reflexion at the surfaces of the particles. The total intensity of radiation scattered by charcoal $\propto$ the square of the λ of the primary rays. J. W. S.

X-Ray reflectivity and resolving power of the (10·0) planes of etched quartz crystals. L. G. PARRATT (Rev. Sci. Instr., 1935, [ii], **6**, 113—115; cf. this vol., 57).—The widths of the (1, −1) rocking curves at half max. intensity, % reflexion, and coeff. of reflexion are tabulated and plotted for λλ 0·56—7·11 Å., including at 6·7 Å. the absorption limit of Si. The main advantage of crystals cut parallel to the (10·0) planes lies in the relatively large grating-space, suiting the crystals to the range 5—8 Å. N. M. B.

Dynamics of molecular crystal lattices. I. Neon. V. DEITZ (J. Franklin Inst., 1935, **219**, 459—469).—The lattice energy of a mol. crystal is considered, and the potential consts. in the equation for the complete lattice energy are evaluated. The method of Morgenau (Physical Rev., 1931, **37**, 1425) is applied for calculating the attraction const. from spectroscopic data. The dynamics of the small vibrations of a face-centred cubic lattice are investigated by Born and Karman's method. A. J. M.

Significance of the persistence of the crystalline state above the m.p. R. E. BURK (Science, 1935, **81**, 344—345).—Theoretical. L. S. T.

Scattering of X-rays by polyatomic gases. S. S. LU (Chinese J. Physics, 1933, **1**, 51—73).—Abs. vals. of the intensity of total scattering, by comparison with that in O_2, are given for Cl_2, CO_2, N_2O, H_2S, CCl_4, and $CHCl_3$ for a range of scattering angles 15—130°, using Mo $K\alpha$ rays separated by balanced ZrO_2 and SrO filters. Results are in agreement with Woo's theory (cf. A., 1932, 892). N. M. B.

Dispersion of X-rays by nickel. I. Atomic-factor curve for nickel. I. UMANSKI and V. VEKSLER (Physikal. Z. Sovietunion, 1934, **6**, 258—267).—Experimental and calc. vals. are compared. CH. ABS. (*e*)

X-Ray diffraction patterns of ice. E. F. BURTON and W. F. OLIVER (Nature, 1935, **135**, 505—506).—X-Ray diffraction patterns of ice formed by condensation of H_2O vapour on Cu at (*a*) −85° and (*b*) at −155° show in case (*a*) lines characteristic of the close-packed hexagonal structure of ice, and in case (*b*) a diffuse line indicating the amorphous character of the condensate. The existence is indicated of a crit. temp., approx. −110°, below which the condensate is vitreous and above which crystals are formed. L. S. T.

Formation of ice crystals. O. BALLY (Helv. Chim. Acta, 1935, **18**, 475—476).—The crystallisation of long needles of ice above the surface of H_2O, under special conditions of temp., wind, etc., is described. E. S. H.

***C*-Modification of neodymium and lanthanum sesquioxides.** K. LÖHBERG (Z. physikal. Chem., 1935, **B**, **28**, 402—407).—Cubic Nd_2O_3 (*a* 11·05 Å.) and La_2O_3 ($a \simeq 11{\cdot}4$ Å.) are *C* modifications. R. C.

Crystal structure of lead chromate produced in the intermicellar space of cellulose. U. YOSHIDA and N. MATSUMOTO (J. Soc. Chem. Ind. Japan, 1935, **38**, 113B).—The $PbCrO_4$ exists as a crystal powder belonging to the tetragonal system, instead of the usual monoclinic system. A. G.

Crystal structure of cæsium enneachlorodithallite, $Cs_3Tl_2Cl_9$. J. L. HOARD and L. GOLDSTEIN (J. Chem. Physics, 1935, **3**, 199—202).—$Cs_3Tl_2Cl_9$ may form uniaxial hexagonal plates or prisms depending on the concns. of CsCl and $TlCl_3$ in the solution from which it crystallises. It is rhombohedral with a_0 9·58 Å. and α 83° 48′, containing 2 mols. Extensive and perfect 60° twinning on the basal plane is shown. The X-ray data indicate approx. closest packing. Tl_2Cl_9''' is regarded as a covalent complex. The structure is compared with that of $Cs_3As_2Cl_9$ and $KMgF_3$. M. S. B.

Structure of methylammonium alum, $NH_3MeAl(SO_4)_2,12H_2O$. H. LIPSON (Phil. Mag., 1935, [vii], **19**, 887—901).—X-Ray data and an electron density map of the salt are given and the interat. distances and dispositions deduced. The NH_3Me appears to be spherically symmetrical. The structure differs from that of K alum, but is apparently similar to that of Cs alum, and the possibility of distinguishing between the external forms of the two structures is suggested. R. S.

Classification of silicates. W. F. DE JONG (Natuurwetensch. Tijds., 1935, **17**, 31—43).—The mineral silicates are classified according to their tetrahedral $[SiO_4]^4$ and $[AlO_4]^5$ structures. S. C.

Crystal structure of common zoisite. L. WALDBAUER and D. C. MCCANN (Amer. Min., 1935, **20**, 106—111; cf. A., 1931, 415).—X-Ray analysis of common translucent zoisite, from Praegratten, Austria, shows that it is made up of a mosaic of submicroscopic multiple twins of clinozoisite (I). (I) has $a:b:c = 8{\cdot}92:5{\cdot}60:10{\cdot}21$; space-group C_2^5 with 2 mols. per unit cell. L. S. T.

Crystal structure of diaspore. F. J. EWING (J. Chem. Physics, 1935, **3**, 203—207).—The unit cell of diaspore has *a* 4·40, *b* 9·39, and *c* 2·84 Å., and contains $4AlHO_2$. The structure is discussed on the basis of the co-ordination theory. The position of the H linkings has been determined. The formula may be written as $(AlHO_2)_n$ or $(HAlO_2)_n$ to admit the known co-ordination no. of 6 for Al. Formulæ suggesting the existence of H_2O or OH′ in the mol. are wrong. M. S. B.

Crystal structure of pyrophyllite, $Al_2(OH)_2Si_4O_{10}$. J. PALACIOS and J. A. BARASOAIN (Anal. Fís. Quím., 1934, **32**, 271—274).—Pyrophyllite is monoclinic (pseudo-hexagonal) with *a* 5·20, *b* 9·06, *c* 18·29 Å., α 95° 41′, 4 mols. per unit cell, *d* 2·77, space-group C_{2h}^3 (possibly C_2^3 or C_s^3). D. R. D.

Crystal structure of chromium, molybdenum, and tungsten hexacarbonyls. W. RÜDORFF and U. HOFMANN (Z. physikal. Chem., 1935, **B**, **28**, 351—370).—These crystallise in the rhombic system, space-group C_{2v}^9, and the unit cell contains four $M(CO)_6$ mols. The dimensions of the unit cell, *a*, *b*, and *c*, are: $Cr(CO)_6$, 11·7$_2$, 6·2$_7$, 10·8$_9$; $Mo(CO)_6$, 12·0$_2$, 6·4$_8$, 11·2$_3$; $W(CO)_6$, 11·9$_0$, 6·4$_2$, 11·2$_7$ Å. In $Cr(CO)_6$ and $Mo(CO)_6$ the distance C–O is 1·15, and the distances Cr–C and Mo–C are 1·80 and 2·13 Å., respectively. The results confirm the assumption that the CO groups surround the metal atom in the form of a regular octahedron, and support Langmuir and

Pauling's views on the co-ordinative atom linking in the carbonyls (A., 1931, 670). R. C.

Cyanuric triazide. (Miss) I. E. Knaggs (J. Chem. Physics, 1935, **3**, 241).—A comparison of the author's data with those of Hughes (this vol., 286). It has been shown that the electron densities at the centres of the atoms rise to > 8 and 10 electrons per sq. Å. for C and N, respectively. M. S. B.

Symmetry and structure of the crystals of the hydrochlorides of triaminotriethylamine. F. M. Jaeger and J. Beintema (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 243—248).—$N(C_2H_4\cdot NH_3Cl)_3$ (cubic) is formed on slow evaporation of a solution of $N(C_2H_4\cdot NH_2)_3$ in very slight excess of HCl; with a larger excess of HCl $N(C_2H_4\cdot NH_3Cl)_3,HCl,H_2O$ (hexagonal) is formed. The *X*-ray spectra of the crystals have been studied. R. S. B.

***X*-Ray investigation of the crystals of anthranilic acid.** M. Prasad and M. R. Kapadia (Indian J. Physics, 1935, **9**, 239—243).—Two types of crystals deposit on slow evaporation of solutions in EtOH. (I) has *a* 16·16, *b* 11·77, *c* 7·17 Å., *d* 1·355, space-group Q_h^{11}. (II) has *a* 12·77, *b* 10·8, *c* 9·403 Å., *d* 1·422, space-group Q_h^5. Each has 8 mols. per unit cell. N. M. B.

Space-group and atomic arrangements in anthraquinone crystals. I. K. Banerjee and B. C. Guha (Indian J. Physics, 1935, **9**, 287—294).—Oscillation-photograph data for rotation about the *b* and *c* axes are tabulated. The space-group is V_h^{13}. N. M. B.

***X*-Ray diffraction from hæmoglobin and other crystalline proteins.** R. W. G. Wyckoff and R. B. Corey (Science, 1935, **81**, 365—366).—*X*-Ray photographs of edestin, excelsin, and hæmoglobin show that these proteins crystallise with H_2O of crystallisation which is readily lost. When this decomp. is prevented, typical powder patterns rich in sharp lines are obtained. Some of the spacings are much > those found with insol. protein structures such as silk, hair, and tendon. L. S. T.

***X*-Ray single-crystal photographs of insulin.** D. Crowfoot (Nature, 1935, **135**, 591—592).—The crystals form flat rhombohedra stable in air. They are simple rhombohedral cells with *a* 44·3 Å. and α 115°; *d* 1·306±0·003, calc. cell mol. wt. 39,300±800. The wt. of insulin in the cell (cell mol. wt.—H_2O of crystallisation) is 37,200. The crystal unit cell appears to contain only 1 mol. of insulin. Each mol. is surrounded by 8 others, 2 at 30 Å. above and below along the trigonal axis and 6 at 44 Å. along the edges of the primitive rhombohedron. The shape of the mol. is approx. an oblate spheroid of diameters 44 and 30 Å. The crystal structure of insulin is compared with that of pepsin. L. S. T.

***X*-Ray rotation crystal and fibrous structure diagrams. IV. White and monochromatic *X*-rays. V. *X*-Ray diagrams of the cellulose micelle.** M. Ishihara (J. Soc. Chem. Ind. Japan, 1935, **38**, 105—107B, 107—110B).—IV. Mathematical. V. Data and photographs are given for hemp cellulose. A. G.

Penetration of pyridine and methyl alcohol into the lattice of cellulose. K. Hutino and I. Sakurada (Bull. Inst. Phys. Chem. Res. Japan, 1935, **14**, 300—302).—The replacement of H_2O in the H_2O–cellulose lattice by C_5H_5N and MeOH has been established by *X*-ray examination. R. S.

Electron diffraction as a method of research. G. P. Thomson (Nature, 1935, **135**, 492—495).—A summary of recent results. L. S. T.

Diffraction of electrons in the determination of the lattice structure of organic compounds. G. Natta, M. Baccaredda, and R. Rigamonti (Gazzetta, 1935, **65**, 182—198).—Electron diffraction measurements have been made with a large no. of highly polymerised org. substances (celluloses, collodions, etc.) and compared with previously recorded data and with the results of *X*-ray measurements. Many of the photograms attributed by previous observers to collodion, celluloid, and other cellulose derivatives are due to very thin films (probably bimol.) of fatty impurities adsorbed on the surface, which can be avoided only by taking very great precautions. O. J. W.

Determination of the structure of simple molecules by electron interference. H. Boersch (Monatsh., 1935, **65**, 311—337).—The results support a linear structure for the mols. of C_3O_2 and COS. CF_4 has a tetrahedral structure. The angle O–F–O in the OF_2 mol. is 100±3°. $(NMe_2)_2$ has a *trans* configuration. CH_2N_2 has a ring structure. Distances between the atoms in these compounds are deduced. E. S. H.

Influence of temperature on the diffraction of slow electrons by a graphite crystal. V. E. Laschkarev and G. A. Kuzmin (Physikal. Z. Sovietunion, 1934, **6**, 211—223).—The temp. dependence is the same for *X*-rays and electrons. The inner potential of graphite is 18—20 volts. Ch. Abs. (*e*)

Absorption factor in electron diffraction. V. E. Laschkarev and A. S. Chaban (Physikal. Z. Sovietunion, 1934, **6**, 205—210).—Relative intensities of Debye lines were measured as a function of the angle of inclination of the oxidised cleavage plane of Mg. The absorption factor is of the same form for electrons and for *X*-rays. Ch. Abs. (*e*)

Magnetic investigations of electromagnet cores of a new type. J. L. Snoek (Physica, 1935, **2**, 403—412).—A Ni–Fe alloy with 30—100% Ni was made anisotropic by first rolling down > 99% and recrystallising. The strip thus obtained behaves as if it were a single crystal with one axis parallel to the strip and one cube face in the surface. This is then rolled down to 30%, when it has a very high magnetic anisotropy in the plane of the strip. Determination of the magnetisation curves in a direction perpendicular to the plane of the strip and observations of the resistance change in a magnetic field indicate that the elementary magnets have min. energy in a direction in the plane of the strip. The permeability in a direction perpendicular to this is very low (35). A. J. M.

Influence of grain size on magnetic properties. W. E. Ruder (Trans. Amer. Soc. Metals, 1934, **22**,

1120—1131).—Although there appears to be a slight relationship between grain size and hysteresis loss, other factors such as strain and purity of the alloys have a much greater influence. Orientation of the crystals is important, and single crystals may give vals. in one direction 100% > in other directions. W. P. R.

Piezometric researches. I. Influence of high pressures on the temperature of fusion and temperature of transformation of organic substances. L. Deffet (Bull. Soc. chim. Belg., 1935, **44**, 41—80, 99—139).—The investigation was carried out at const. vol. in a special apparatus. The sources of error are discussed and fusion pressures (I) up to 1000 kg. per sq. cm., corresponding with a series of temp., are given for CCl_4, $MeNO_2$, C_2HCl_5, $C_2H_4Br_2$, $Bu^{\gamma}OH$, *tert.*-C_5H_{11}·OH, HCO_2H, AcOH, $EtCO_2H$, $Pr^{\alpha}CO_2H$, $Bu^{\alpha}CO_2H$, *n*-hexoic, *n*-heptoic, and *n*-octoic acids, $HCO{\cdot}NH_2$, *cyclo*hexane, C_6H_6, $PhNO_2$, *m*-and *p*-$C_6H_4Me{\cdot}NO_2$, *o*- and *p*-xylene, PhOH, *m*-cresol, $COPh_2$, MeOBz, PhCN, NH_2Ph, $NPhMe_2$, *p*-$C_6H_4Me{\cdot}NH_2$, and piperidine. The transition pressures and (I) of a no. of enantiomorphs have been studied over the same range: *n*-cetyl alcohol, transition point at atm. pressure (t.p.) 43·6—44·1°; *n*-dotriacontane, t.p. 64·3°; methyl*cyclo*pentanol, t.p. 29·15°, triple point at 2000 kg. per sq. cm. and 72°; MeOBz, t.p. 16·8°. The m.p. and (I) data are recorded for the monotropes: *n*-cetyl iodide, *o*-$C_6H_4Me{\cdot}NO_2$, *o*-$C_6H_4Me{\cdot}NH_2$, Ph salicylate (II), CH_2I_2, including a new form of (II). Vals. of $\delta=1+\Delta V/L$, where L is the latent heat of fusion and ΔV the difference between the sp. vol. of solid and liquid, have been calc. for a large no. of substances and good agreement was obtained with experiment. The relation between δ and various properties is discussed. R. S.

Relation between fusion and strength. H. Jeffreys (Phil. Mag., 1935, [vii], **19**, 840—846).—The strength of materials forming the earth's crust is discussed from the point of view of the pressure required to lower the m.p. to the ordinary temp. For substances for which the necessary data are available the actual crushing strength is < that calc., although the order (of increasing or decreasing strength) is correctly given. F. L. U.

Energy and elastic constants of some heteropolar crystals. V.Ždanov, A. Erschov, and G. Galachov (Z. Physik, 1935, **94**, 241—249).—Wave-mechanics calculations are given for alkali halide crystals. A. B. D. C.

Hume-Rothery rule for intermetallic compounds. U. Dehlinger (Z. Physik, 1935, **94**, 231—240).—Bloch's theory of metals leads to the Hume-Rothery rule. A. B. D. C.

Rotational and translational degrees of freedom in the solid state. New conceptions concerning the structure of solids. II. J. A. A. Ketelaar (Chem. Weekblad, 1935, **32**, 262—270).—A review. D. R. D.

Influence of mechanical deformation on the transformation velocity of polymorphic metals. E. Cohen, W. A. T. Cohen-de Meester, and A. K. W. A. van Lieshout (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 377—387).—The velocity of transformation, v, of white to grey Sn at −50° is greatly increased by rolling, drawing, or cracking the white Sn, v increasing with the degree of deformation. Deformation at −80° gives a higher v at −50° than deformation at room temp. Tempering at 150° after deforming greatly reduces v. R. S. B.

Rate of polymorphic transformations. I. Tin plague. II. E. Cohen and A. K. W. A. van Lieshout (Z. physikal. Chem., 1935, **173**, 1—31, 67—70).—I. The rate of transformation of grey into white Sn under xylene at 25·6° passes through a max. with increase in the no. of times which the specimen has been converted previously from one form into the other, and is especially affected by the temp. at which the preceding transformation into white Sn occurred. The rate is a max. when ~ 30% of white Sn has been formed. At 25·6° the rate of conversion of grey Sn which has previously been repeatedly converted in air is negligible. Such inactive Sn may, however, be rendered active again, and then undergoes reversible undelayed transformation at a measurable rate even near the transition point. Shaking during transformation of grey into white Sn causes great acceleration. The rate also depends on the previous thermal and mechanical treatment of the Sn. The results in conjunction with van Arkel and Koets' observations (A., 1927, 401) afford a general explanation of the delay and other phenomena associated with the transformation of Sn.

II. The "region of indifference" reported for various polymorphic transformations (Bridgman, Proc. Amer. Acad. Sci., 1916, **52**, 57) is a purely accidental effect, depending on the previous treatment of the substance examined, and by appropriate variation of that treatment may be eliminated. Its elimination has been achieved for Sn and NH_4NO_3. R. C.

Physico-chemical studies on tin. X. Transition temperature grey tin ⇌ white tin. E. Cohen and A. K. W. A. van Lieshout (Z. physikal. Chem., 1935, **173**, 32—34).—By experiments with Sn activated so as to undergo reversible undelayed transformation in the immediate vicinity of the transition point (cf. preceding abstract) the latter has been found to be 13·2±0·1°. R. C.

Transition of potassium superoxide. E. W. Neuman (J. Chem. Physics, 1935, **3**, 243).—Heating and cooling curves for KO_2 show a break at −75·5± 0·5°. A colour change from deep orange to light cream occurs on cooling at approx. the same temp. It is not possible, by the method employed, to distinguish between a true polymorphic transition and a gradual one. M. S. B.

Mol. wts. of cellulose and cellulose derivatives. E. O. Kraemer and W. D. Lansing (J. Physical Chem., 1935, **39**, 153—168).—Different methods for determining the mol. wt. of cellulose and its derivatives, and the relation between mol. wt. and viscosity, η, are discussed. There is a definite parallelism between degree of polymerisation of linear mols., such as cellulose, and the quantity $[\eta]=\lim_{c\to 0}(\eta_r-1)/c$, where η_r is the ratio of $\eta_{solution}$ to $\eta_{solvent}$ at concn. c g. per 100 c.c. of solution. The ultra-centrifuge

method of mol. wt. determination gives more detailed information as to distribution of mol. wts. etc. than any other method. M. S. B.

Mol. wts. of the phthalocyanines. J. M. Robertson, R. P. Linstead, and C. E. Dent (Nature, 1935, **135**, 506—507).—Ni, Cu, and Pt phthalocyanines have *a* 19·9, 19·6, 23·9 Å., *b* 4·71, 4·79, 3·81 Å., *c* 14·9, 14·6, 16·9 Å., β 121·9°, 120·6°, 129·6°, respectively, 2 mols. per unit cell, space-group C_{2h}^5 ($P2_1/a$) and max. mol. wts. 586, 583, and 712, respectively. The min. mol. wts. from elementary analyses coincide with these vals. and hence the formula is $C_{32}H_{16}N_8M$, where M is the metal atom which must reside at the centre of symmetry, and the mol. wts. calc. from the formulæ are 571, 576, and 707, respectively. The cell dimensions show that the large flat mols. must be well spread out in the *ac* plane. The vals. of *d*, determined by flotation methods, are 1·63, 1·63, and 1·98, respectively, and the mol. vols. are practically const. L. S. T.

Magnetic susceptibility of lithium hydride. Diamagnetism of ionic crystals. S. Freed and H. G. Thode (J. Chem. Physics, 1935, **3**, 212—215).—The mol. magnetic susceptibility of LiH at 300° and 78° abs. is $-4·60\times10^{-6}$ with practically no temp. coeff. Deviations from theoretical vals. are ascribed to a paramagnetism present in all crystals, not included in the calculation. M. S. B.

Magnetic susceptibility of cadmium compounds. W. R. A. Hollens and J. F. Spencer (J.C.S., 1935, 495—496).—Mass susceptibilities of 30 Cd compounds are recorded. Cd has at. susceptibility $-24·85\times10^{-6}$. *Cd borofluoride* is described. F. L. U.

Magneto-chemical investigations of organic compounds. I. Existence of diradicals. E. Müller and I. Müller-Rodloff (Annalen, 1935, **517**, 134—151).—Magnetic examination of 4 : 4′- (Tschitschibabin, A., 1907, i, 503) and 3 : 3′-diphenylenebisdiphenylmethyl (I) (Schlenk *et al.*, A., 1915, i, 519), 2 : 3-6 : 7-dibenzanthracene, tetraphenylrubene, diphenyldiazomethane, and 4 : 4′-bisbenzhydryl-αβ-diphenylethane shows that the existence of a C diradical can be detected only in the case of (I). Formation of a quinonoid system occurs whenever possible and diradicals can be detected only where such valency tautomerism is impossible. True diradicals can be expected only when there is no possibility of intermol. stabilisation (*ortho* compounds) or when the transition to a valency tautomeric, quinonoid system is excluded. Although magneto-chemical examination disproves the presence of considerable amounts of diradicals in the compounds mentioned above, it does not preclude the existence of amounts $<$ 1—2% in equilibrium with the less reactive form; it is not expedient, however, to ascribe to these compounds a radical structure, since the bulk of the material exists in a normal quinonoid state. H. W.

Magnetic susceptibility of tetraphenylrubene and of its dissociable oxide. L. Enderlin (Compt. rend., 1935, **200**, 912—914).—The mol. susceptibilities of tetraphenylrubene (I) and of its oxide (II) are -3440 and -3525 ($\times10^{-7}$), respectively, whereas the vals. calc. on the basis of the generally accepted formula for (I) and Dufraisse's formula for (II) (A., 1933, 1284) are -3500 and -3662 ($\times10^{-7}$). The results indicate that the O are attached to the nucleus by normal linkings. J. W. S.

Diamagnetic susceptibility of water polymerides. L. Sibaiya (Current Sci., 1935, **3**, 421—422).—Vals. for $\chi_{20°}$ are calc. for H_2O, $(H_2O)_2$, and $(H_2O)_3$ assuming the relative abundance given by Rao (cf. A., 1934, 942) from Raman spectra. The calc. vals. are compared with experimental data and discussed from the point of view of the additivity law and O valency. W. R. A.

Adiabatic demagnetisation of some paramagnetic salts. W. J. de Haas and E. C. Wiersma (Physica, 1935, **2**, 335—340).—The effect of the magnetic field strength on the temp. reached by adiabatic demagnetisation was investigated for Fe NH_4 alum, $Ce(EtSO_4)_3,9H_2O$, and K Cr alum mixed with 14·4 mols. of K Al alum. Fe NH_4 alum is a very suitable substance for reaching very low temp. $Ce(EtSO_4)_3$ is not so suitable. There is a considerable increase in the sp. heat of this substance in the neighbourhood of 0·1° abs. There is no effect of alteration of field strength. The dil. K Cr alum gave a temp. of 0·0044° abs., the lowest yet recorded. A. J. M.

Thermo-electric effect with palladium–silver alloys charged with hydrogen. J. Schniedermann (Ann. Physik, 1935, [v], **22**, 425—442).—The thermo-electric effect (I) (electron emission) of all Pd–Ag alloys is increased when they are charged with H_2. The 60% Pd–40% Ag alloy shows min. (I) both when uncharged and when charged with H_2; it also shows the min. Hall effect and electrical conductivity. The increase in (I) on absorption of H_2 is due both to an increase in the no. of free electrons and to a decrease in the emission work, as is shown by the deviations of these alloys from the Richardson law. A summary of the physical properties of Pd–Ag alloys, both with and without adsorption of H_2, is given. A. J. M.

Thermo-electric power and resistance. L. Nordheim and C. J. Gorter (Physica, 1935, **2**, 383—390).—The general theory of thermo-electric power (I) is discussed with reference to the parallelism between (I) and resistance. The effect of impurities (solid solutions) is considered. The disturbance in a ferromagnetic material may be regarded as a mixture effect. A. J. M.

Superconductivity and diamagnetism. F. London and H. London (Physica, 1935, **2**, 341—354).—Theoretical. The super-current is regarded as a kind of diamagnetic vol. current, maintained by a magnetic field, which may be produced by the current itself. A. J. M.

Magnetic properties and critical currents of superconducting alloys. J. N. Rjabinin and L. W. Shubnikow (Nature, 1935, **135**, 581—582).—The relation between field strength and the magnetic induction at 2·11° abs. for a Pb–Tl alloy corresponding in composition with $PbTl_2$, and a Pb–Bi alloy (65% Pb) is described. Superconductivity is lost above a certain crit. field strength. L. S. T.

Electromagnetic equations of the superconductor. F. London and H. London (Proc.

Roy. Soc., 1935, **A**, **149**, 71—88).—Mathematical. A new formulation of the dependence of current on field in superconductors is established. L. L. B.

Optical measurements of ultrasonic wave velocities in liquids. C. Bachem and E. Hiedemann (Z. Physik, 1935, **94**, 68—71).—Measurements are given for PhMe, C_6H_6, CCl_4, and *m*-xylene. A. B. D. C.

Influence of ultrasonic waves on some physico-chemical properties. L. Hauss (Bull. Soc. chim. Belg., 1935, **44**, 154—166; cf. this vol., 573).—Effects produced are discussed. The velocity of deposition of a suspensoid is diminished by ultrasonic waves. R. S.

Velocity of elastic waves in the mercury crystal and the characteristic temperature calculated therefrom. E. Grüneisen and H. Hoyer (Ann. Physik, 1935, [v], **22**, 663—673).—The theory of the velocity of elastic waves (I) in trigonal crystals is given. (I) in the Hg crystal was determined by calculating the velocities of sound for a no. of directions in the crystal. The wave surface in Hg is similar to that in quartz. The Debye characteristic temp. ($\theta_{elast.}$) in the range over which the T^3 law holds is 68·6°. Comparison with θ_D shows greater agreement than is the case for Zn or Cd. At higher temp. $\theta_{elast.} < \theta_D$ for Hg, but the reverse is the case for Zn and Cd. A. J. M.

Theory of specific heat. III. Existence of pseudo-T^3 regions in the specific heat curve of a crystal. IV. Calculation of the specific heat of crystals from elastic data. M. Blackman (Proc. Roy. Soc., 1935, **A**, **149**, 117—125, 126—130; cf. this vol., 573).—III. The possibility of pseudo-T^3 regions in the sp. heat curve is deduced from the general form of the vibrational spectrum of a cubical lattice. The theory explains the discrepancies hitherto found between the θ_D vals. derived from thermal and from elastic data at low temp.

IV. A new method, based on considerations of lattice theory and on the geometrical form of the wave surfaces, is deduced, by which θ_D vals. can be calc. from elastic data. L. L. D.

Heat content of water and water vapour. W. Koch (Z. Ver. deuts. Ing., 1934, **78**, 1160; Chem. Zentr., 1934, ii, 3602).—Data are tabulated. H. J. E.

Heat capacity curves of the simpler gases. VII. High-temperature heat capacities of oxygen and influence of the $^1\Delta$ level on the thermodynamic properties of the gas. H. L. Johnston and M. K. Walker (J. Amer. Chem. Soc., 1935, **57**, 682—684; cf. A., 1934, 1300).—Vals. of heat capacity, entropy, free energy, and dissociation of O_2, based on spectroscopic data, are revised in accordance with the existence of the $^1\Delta$ electronic state. The influence of the $^1\Delta$ term is insignificant below 3000° abs. for the dissociation, and contributes $< 0·002$ g.-cal. to the mol. free energy function below 1750°; to the mol. entropy below 1250°; and to the mol. heat capacity below 1000°. The $^1\Delta$ contribution to the heat capacity attains a max. of nearly 0·6 g.-cal. at about 4500° abs. E. S. H.

Critique of the electrical differential method for the measurement of C_v for gases. VI. Specific heats of argon and air. M. Trautz and A. Reichle (Ann. Physik, 1935, [v], **22**, 513—524).—Improvements in the method previously used (A., 1927, 817) are described. C_v for air is 4·951 g.-cal.$_{16}$ per degree, referred to zero pressure. A. J. M.

Specific heat of iron–carbon systems at high temperatures, and the heat changes accompanying those of phase. S. Umino (Sci. Rep. Tôhoku, 1935, **23**, 665—793).—The heat content and mean and true sp. heat of 19 Fe–C alloys (0·07—5·07% C) were found by the method of mixtures at various temp. up to > m.p. The heat content and sp. heat of cementite at high temp. were found by extrapolation. Data and curves are given for heats of dissolution of one form in another, heats of transition, and latent heats of fusion. N. M. B.

True specific heat of some metals and alloys. K. Honda and M. Tokunaga (Sci. Rep. Tôhoku, 1935, **23**, 816—834).—Using an improved Nernst–Lindemann electrical method sp. heats were measured for Cu, Al, Fe, Mg, Cu–Ni, Mg–Zn, Mg–Al, Al–Cu, duralumin, brass, and bronze. The additive law was not obeyed by the alloys except in the case of bronze and brass (70% Cu). Brass (60% Cu) does not obey the law. N. M. B.

Specific heat of certain minerals and salts of the rare-earth elements. W. Swientosławski, J. Salcewicz, J. Usakiewicz, A. Zmaczyński, and J. Złotowski (Rocz. Chem., 1935, **15**, 12—14).—The vals., determined in an ice calorimeter, are: Ag, c_7 0·05532, Sb, c_7 0·04745, johannite, $c_{7·5}$ 0·1290, thorite, c_7 0·1320, samarskite, c_8 0·1078, monazite, $c_{18·9}$ 0·1024, $ScF_3,3NH_4F$, $c_{7·7}$ 0·4223, $Y(NO_3)_3$, $c_{7·8}$ 0·2752, $La(NO_3)_3,6H_2O$, $c_{7·8}$ 0·2713, $Y_2(C_2O_4)_3,12H_2O$, $c_{8·4}$ 0·4640, $La_2(C_2O_4)_3,10·5H_2O$, $c_{8·4}$ 0·2647, sucrose, $c_{7·5}$ 0·2774. R. T.

Molecular latent heats. J. D. Huffington (Phil. Mag., 1935, [vii], **19**, 836—840).—Putting the const. of Trouton's rule$=CR \log (v_1/v_2)$, where v_1 and v_2 are vols. of saturated vapour and of liquid, it is shown that C is a definite function of L/T (L= mol. heat of vaporisation, T=abs. temp.). A table of vals. for 21 substances is given. F. L. U.

Heats of fusion and transformation of 1 : 4-dioxan. W. A. Roth and I. Meyer (Z. Elektrochem., 1935, **41**, 229—231; cf. A., 1933, 217).—Heats of fusion and of transformation of dioxan are, respectively, 34·25 and 6·32 g.-cal. per g. Dioxan undergoes a slow spontaneous change and is not suitable for use as a cryoscopic solvent. F. L. U.

Accommodation coefficient and the evaporation coefficient of water. T. Alty and C. A. Mackay (Proc. Roy. Soc., 1935, **A**, **149**, 104—116).—Experiments are described in which H_2O vapour mols. are incident on a liquid surface of which the temp. is < that of the vapour, and the energy transferred to the surface by the vapour mols. is measured. For H_2O at 10°, the evaporation coeff. is 0·036, the accommodation coeff. 1·0, indicating that, while only a small fraction of the vapour mols. enters the

liquid, all of them reach temp. equilibrium with the surface before re-evaporating into the vapour. L. L. B.

Theory and laws of vaporisation. A. Missenard (Chaleur et Ind., 1934, **15**, 129—141; Chem. Zentr., 1934, ii, 3601).—A discussion of the relation between vaporisation and convection. H. J. E.

Density of water from various sources and isotopic ratio in hydrogen. J. N. Rakshit (J. Physical Chem., 1935, **39**, 303).—It is suggested that the possible influence of the polymerisation of H_2O should be considered in the determination of the isotopic ratio of H_2 from very accurate d measurements of H_2O. M. S. B.

Vapour pressure of neon at liquid hydrogen temperatures. W. H. Keesom and J. Haantjes (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 376).—The v.p. of Ne at 15—20·4° abs. is given by $\log_{10} p(\text{cm.}) = -111{\cdot}76/T + 6{\cdot}0424$, and agrees with vals. calc. by the theory for a monat. substance, with a heat of vaporisation at 0° abs. of 445·9 g.-cal. per mol. R. S. B.

Vapour-pressure curve of formaldehyde, and related data. R. Spence and W. Wild (J.C.S., 1935, 506—509; cf. this vol., 608).—The v.-p. curve for CH_2O has been traced from the m.p. (−118°) to the b.p. (−19·2°). The heat of vaporisation $= 6545 + 3{\cdot}480T - 0{\cdot}02885T^2$. Trouton's const. = 21·9 entropy units. CH_2O is a normal liquid. Polymerisation occurs only at a solid surface, and the polymeride is so insol. in the liquid that the v.p. of the latter is unaffected. F. L. U.

Elementary derivation of the statistical fundamental formulæ of chemical thermodynamics. G. Schubin (Compt. rend. Acad. Sci. U.R.S.S., 1935, **1**, 301—304).—Theoretical. Statistical-mechanical distribution formulæ have been derived for classical, Bose–Einstein, and Fermi–Dirac statistics. R. S. B.

Boyle's law in the new theory of the equation of state. V. Jacyna, S. Derevjankin, A. Obnorski, and T. Parfentjev (Z. Physik, 1935, **94**, 224—228). A. B. D. C.

Foundation of thermodynamics. F. von Krbek (Z. Physik, 1935, **94**, 204—210).—Theoretical. The equation of state for ideal gases is considered. A. B. D. C.

Equation of state of real gases. W. Fritz (Physikal. Z., 1935, **36**, 217—220).—The thermodynamic bases of the Honigmann equation of state (A., 1931, 31), and of the adiabatic equations, $pv^n = \text{const.}$ and $Tp^{-(n-1)/n} = \text{const.}$, are examined, and it is shown that these equations contradict certain important thermodynamic requirements. A. J. M.

Definition of the Gibbs potential. J. N. Brönsted (J. Chem. Physics, 1935, **3**, 223).—Explanation of an earlier reference to Gillespie and Coe's work on the physical interpretation of the chemical potential (cf. A., 1933, 217). M. S. B.

Nernst's heat theorem. V. Njegovan (Z. Physik, 1935, **94**, 377—385).—Inadequacies of the third heat theorem can be overcome by choosing consts. suited to the phenomena involved. A. B. D. C.

Calculation of physical properties of the rare gases from the Clausius virial. E. Brander (Soc. Sci. fenn., Comment. phys.-math., 1934, **7**, No. 14, 9 pp.; Chem Zentr., 1934, ii, 3601—3602).—Calc. vals. for b (in c.c.) are Ne 0·000930, A 0·00253, Kr 0·00341, Xe 0·00486. The at. radii are 1·25—1·27, 1·63—1·77, 1·86—1·96, and 2·13—2·20 ($\times 10^{-8}$) cm., respectively. H. J. E.

Critical temperature of heavy water. E. H. Riesenfeld and T. L. Chang (Z. physikal. Chem., 1935, **B**, **28**, 408—409).—The crit. temp. of D_2O is 371·5°. R. C.

Effect of temperature on the thermal conductivity and the accommodation coefficient of hydrogen. H. S. Gregory (Proc. Roy. Soc., 1935, **A**, **149**, 35—56).—Using a modification of the hot-wire method, in which the influence of convection and the temp. fall effect are eliminated in one operation, vals. have been obtained of the thermal conductivity K of H_2, varying from 459×10^6 to 708×10^6 g.-cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$ at 295·1° and 593·4° abs., respectively, and of the accommodation coeff. f for the H_2–Pt phase. The variation of K with temp. is given by $K_T = AT^n$. f has a min. val. of 0·21 at 520° abs. and is independent of pressure over the range considered. L. L. B.

Thermal conductivity of deuterium. A. B. van Cleave and O. Maass (Canad. J. Res., 1935, **12**, 372—376).—The relative thermal conductivities of D_2 and of D_2–H_2 mixtures, as measured by the hot-wire method, agree with the conclusion that D_2 has the same mol. diameter as H_2 (cf. this vol., 432). It follows that the mol. heats are the same. J. W. S.

Thermal conductivity of polyatomic gases. A. R. Ubbelohde (J. Chem. Physics, 1935, **3**, 219—223).—It is shown that the thermal conductivity of polyat. gases may vary with pressure. A comparison between experimental and calc. data relating to heat transport suggests that a portion of the sp. heat at 0° has, probably, a relaxation const. considerably $< 10^6$ if discrepancies are due to restrictions on the energy exchange between mols. For such cases measurements of heat conductivity between parallel plates are probably preferable to the use of a vertical wire. M. S. B.

Thermal conductivity and accommodation coefficient of carbon dioxide. C. T. Archer (Phil. Mag., 1935, [vii], **19**, 901—918).—Contrary to Ibbs and Wakeman (A., 1932, 216), the thermal conductivity of CO_2 increases continuously from $3{\cdot}47 \times 10^{-5}$ g.-cal. at 0° to $8{\cdot}94 \times 10^{-5}$ at 318·8° according to $K_T = CT^{1{\cdot}216}$. Vals. of the accommodation coeff. from 0·51 at 24·2° to 0·28 at 331·8° are given. R. S.

Change of thermal conductivity of non-polar gases, of liquids, and solids owing to an electric field. G. Groetzinger and R. Frey (Physikal. Z., 1935, **36**, 292—297).—The hot-wire method of Schleiermacher was used to find the thermal conductivity (I) of air in an electric field. There was no effect up to a field strength of 120,000 volts per cm., but above this there was a rapid cooling of the wire due to ionisation. This is contrary to the results of

Senftleben (A., 1932, 328; see following abstract). The addition of small quantities of polar gases causes variation of (I) with weak fields. Liquids such as paraffin and petroleum, which do not show electrolytic conduction (II), give a considerable increase in (I) on application of a field. For solids not showing (II) (BzOH, paraffin wax, S, and colophony) the application of a field does not affect (I), but for solids showing (II), *e.g.*, *m*-$NO_2 \cdot C_6H_4 \cdot NH_2$, there is a fall in the temp. of the wire even with weak fields. A. J. M.

Change of thermal conductivity of non-polar gases, of liquids and solids owing to an electric field. H. Senftleben (Physikal. Z., 1935, **36**, 297—298).—As the apparatus in earlier experiments (A., 1932, 328) was arranged differently from that of Groetzinger and Frey (preceding abstract), it is considered that the results are not at variance. A. J. M.

Heat-conductivity of simple cubical crystals. M. Blackman (Phil. Mag., 1935, [vii], **19**, 989—998).—The theory of Peierls (A., 1930, 282) is discussed. R. S.

Effect of cold-working on thermal conductivity. G. Tammann and W. Boehme (Ann. Physik, 1935, [v], **22**, 500—506).—The % decrease of thermal conductivity (I) produced by cold-working of Fe, Ni, Cu, and Ag is equal to the % decrease of electrical conductivity due to the same cause. Both properties recover from the cold-working effect in the same temp. range. For the alloys 77% Ag–23% Zn and 72% Cu–28% Zn (II), the curve shows two recovery intervals, that at higher temp. being due to Ag or Cu, and at lower temp. to Zn. Plates were heated electrically at a point, and the diameters of the rings produced were measured. These diameters, measured parallel and perpendicular to the direction of rolling, were identical within the limits of experimental error. For (II) there were, however, differences in (I) of about 5%. A. J. M.

Comparison of viscosity data. F. T. Miles (J. Amer. Chem. Soc., 1935, **57**, 698—699).—The correlation of the ratio η at m.p. to η at b.p. with mol. symmetry (cf. A., 1934, 1165) is due largely to the dependence of m.p. on mol. symmetry. E. S. H.

Theory of structure viscosity. I. W. Philippoff (Kolloid-Z., 1935, **71**, 1—16).—The relation $\eta' = \eta_\infty + \eta_0 - \eta_\infty/(1+P^2/\gamma^2)$ is confirmed, mainly by the analysis of published work. Methods of determining the consts. have been worked out. E. S. H.

Diffusion of gases. W. Roth (Arch. Eisenhüttenw., 1934—1935, **8**, 401—403).—Mathematical. Equations are given for calculating the diffusion of various common gases into one another and the effect thereon of temp., pressure, *d*, and mol. wt. Various diffusion coeff. are tabulated and some practical examples of their use are given. A. R. P.

Mutual diffusion of gases at high pressures. B. Kries and N. Seljakov (Z. Physik, 1935, **94**, 134—138).—Theoretical. Numerical examples are given for CO_2 and air. A. B. D. C.

Diffusion of hydrogen in palladium. B. Duhm (Z. Physik, 1935, **94**, 434—456).—Diffusion measurements afford evidence of true dissolution under certain conditions, and vals. for the diffusion coeff. and mobility are recorded. The ratio of these gives the effective proton charge in Pd as a fraction of the elementary charge. A. B. D. C.

Diffusion of hydrogen through aluminium. C. J. Smithells and C. E. Ransley (Nature, 1935, **135**, 548).—H_2 diffuses through Al at a rate which is easily measurable above 400°. The rate is given by $D = k\sqrt{P} \cdot e^{-b/T}$, where *b* is approx. 14,000. At 400—600°, the rate of diffusion is of the same order as that of H_2 through Cu, but the temp. coeff. is greater. L. S. T.

Diffusion of non-metallic elements in iron and steel. I. Diffusion of sulphur in iron and steel. II. Diffusion of oxygen in iron. A. Bramley and F. W. Haywood. **III. Diffusion of phosphorus in iron and steel.** A. Bramley and A. T. Cooper. **IV. Nitriding of iron and steel.** A. Bramley and J. T. Watts (Trans. Faraday Soc., 1935, **31**, 707—713, 713—717, 717—726, 726—734; cf. B., 1932, 386).—I. The rate of diffusion (*D*) of S in Fe is in accordance with Fick's law. In steel, the *D* of S and C are lowered by the presence of the other element.

II. The *D* of O in Fe is approx. 0·005 of that of C at the same temp. The presence of dissolved FeO lowers the *D* of C, but to a smaller extent than does S.

III. The abnormal shape of the [P]–depth curve obtained when P diffuses into Fe and steel may be due to an allotropic change in the metal. This explanation is supported by Haughton's Fe–P equilibrium diagram. The *D* of P in Fe $< 0{\cdot}01$ of that of C, and is lowered further by addition of C. High P content has little influence on the *D* of C.

IV. Fe and steel are nitrided by heating at 850—1100° in N_2 containing NH_3 to an extent depending on the amount of O_2 in the gas or dissolved oxide in the metal. The max. effect is obtained when the nitriding atm. contains 2% of O_2. The presence on the surface of the slightest trace of crystals of Fe oxide completely inhibits nitriding in an atm. of NH_3. The *D* of the N increases with [dissolved oxide]. F. L. U.

Mixed crystal formation and lattice constants for silver–copper alloys. P. Wiest (Z. Physik, 1935, **94**, 176—183).—The solubility of Ag at 600° is 0·6% greater for single than for mixed crystals; the difference increases with fall of temp. A. B. D. C.

Metals and alloys. XIII. Constitution of lithium–cadmium alloys. E. Zintl and A. Schneider. **XIV. Constitution of lithium–bismuth alloys.** E. Zintl and G. Brauer (Z. Elektrochem., 1935, **41**, 294—297, 297—303).—XIII. *X*-Ray analysis indicates the existence of four different crystal types in the system Li–Cd. This confirms the observations of Grube *et al.* (A., 1933, 18) by other methods. The β-phase is stable at higher temp. only, and probably has a cubic symmetry. It is formed from the β′-phase, which has a homogeneity region close to $LiCd_3$ and hexagonal structure, *a* 3·083 Å., *c* 4·889 Å., with 2 atoms per cell and statistical at. distribution.

The mixture phase between β′ and α, or Cd saturated with Li, shows two types of hexagonal packing with axial ratios, one > 1·8 and the other approx. 1·63, which is the ideal val. for closest packing. The γ-phase, LiCd, has a space-centred structure of the NaTl type, *a* 6·687 Å., and the γ′-phase, Li_3Cd, has a face-centred cubic lattice, *a* 4·250 Å., and statistical at. distribution.

XIV. *X*-Ray analysis gives results in agreement with those of Grube *et al.* (A., 1934, 724). Two stable forms are observed at room temp., α-LiBi, tetragonal space-centred, *a* 3·361, *c* 4·247 Å., and Li_3Bi, cubic, *a* 6·708 Å., 16 atoms in the cell. M. S. B.

Hardness study of transformations in gold–copper alloys. H. H. Asher (J. Dental Res., 1934, **14**, 349—358).—The Cu–Au system is an unbroken series of solid solutions with 1 major and 2 minor lattice changes, which are affected by heat-treatment. Ch. Abs. (*e*)

Widmannstätten structure. VII. Copper–silver system. C. S. Barrett, H. F. Kaiser, and R. F. Mehl (Amer. Inst. Min. Met. Eng., Inst. Metals Div., 1935, Tech. Pub. 595, 19 pp.).—A Widmannstätten figure (I) may be formed in Cu-rich Cu–Ag alloys (II) by extremely slow cooling. The Ag-rich ppt. occurs as plates parallel to {100} planes of the Cu-rich matrix. The ppt. in Ag-rich (II) is usually a pearlite-like arrangement of irregular plates. By extremely slow cooling a (I) may be developed in which the Cu-rich ppt. forms plates parallel to the {111} planes of the matrix. The mechanism of formation of (I) is discussed. Ch. Abs. (*e*)

Texture of rolled α-brass. V. I. Iveronova and G. S. Zhdanov (Tech. Physics U.S.S.R., 1934, **1**, 64—79; J. Tech. Phys. U.S.S.R., 1934, **5**, 911—924).—The *X*-ray structure of brass is a function of the Zn content, the stable configuration starting at 10% Zn. The Zn changes the orientations of the (111) and (100) axes, but not the (112) axis. Ch. Abs. (*e*)

***X*-Ray investigations on α-tin bronzes.** T. Isawa and I. Obinata (Mem. Ryojun Coll. Eng., Inouye Com. Vol., 1934, 235—242).—The solubility of Sn in Cu increases from 13·9% at < 400° to a max. of 15·9% at the eutectoid temp. (*T*) (530°) and then decreases to 14·45% at 750°. Tempering of the saturated solid solution quenched from *T* results in a slow separation of the excess of Sn accompanied by lattice distortion. A. R. P.

Transformations in iron–aluminium alloys. C. Sykes and H. Evans (Iron and Steel Inst., May, 1935. Advance copy, 23 pp.).—When alloys of Al and Fe near to Fe_3Al are slowly cooled, the lattice structure changes from a disordered to an ordered type with the evolution of heat beginning at 560° and extending over a wide temp. range, probably down to 200—250°; the crit. temp. determined by the thermal method has been confirmed by resistivity measurements on samples quenched from various temp. Magnetic curves for Fe_3Al slowly cooled from 600° show a sharp max. at about 540°, but this is absent from heating curves. The magnetic transformation curve for ordered alloys with 13—17% Al is below that for disordered alloys, the transformation of the 14% Al alloy occurring at 560° in the disordered and at 490° in the ordered state. A. R. P.

Eutectoid transformation of the aluminium–zinc system. H. Imai and M. Hagiya (Mem. Ryojun Coll. Eng., Inouye Comm. Vol., 1934, 83—105).—The $\beta \longrightarrow \alpha+\gamma$ transformation in the 21% Al alloy takes place at 270°; after quenching from higher temp. a spontaneous heat evolution occurs, the temp. rising by 50° in 3·5 min., accompanied by a contraction which is very rapid during the first min. The resistance (*R*) rises rapidly for 2·5 min. after quenching, then slowly for another min., and finally decreases slowly. Max. hardness (*H*) is reached 13 min. after quenching, and after 15 min. a second evolution of heat occurs with a slight contraction in vol., a slight increase in *R*, and an abrupt decrease of *H*. Min. *H* is obtained in 1 hr. at 100° and normal *R* by storage for 1 month at room temp. or by slowly heating to 150°. These results indicate that the decomp. of β proceeds in 3 stages, $\beta \longrightarrow \beta'$ occurring rapidly and $\beta' \longrightarrow \beta''$ slowly at room temp., whilst $\beta'' \longrightarrow \alpha+\gamma$ occurs only on tempering at just below the eutectoid temp. A. R. P.

Hall effect and other physical constants of alloys. IV. Bismuth–cadmium series. S. Gabe and E. J. Evans (Phil. Mag., 1935, [vii], **19**, 773—787; cf. A., 1934, 137).—Property–composition diagrams are given for sp. resistance, temp. coeff. of resistance, thermoelectric power, Hall coeff., density, and sp. heat. The curves for the two last are linear, and all are continuous. Properties involving the passage of electric current show rapid variations at the Bi end, but there is no definite evidence of the existence in this region of a solid solution. F. L. U.

Solidification diagrams of alloys formed by two alkali metals : potassium–rubidium alloys. E. Rinck (Compt. rend., 1935, **200**, 1205—1206; cf. A., 1933, 771; this vol., 22).—K and Rb form a complete range of mixed crystals. The liquidus and solidus curves are very close and show a min. at K+2Rb. J. W. S.

Solid solubility of silicon in aluminium. S. Kishino (J. Chem. Soc. Japan., 1934, **55**, 1134—1139; cf. B., 1934, 1106).—Structural changes in Al–Si alloys quenched at various temp. have been studied by measurements of electrical resistance. Al dissolves 0·70% of Si at 502° and 1·19% at 545° to form a solid solution. Ch. Abs. (*e*)

Eutectoid iron–cementite diagram. J. Seigle (Bull. Assoc. tech. Fond., 1934, **8**, 289—296; Chem. Zentr., 1934, ii, 3668).—Modifications of the equilibrium diagram are suggested. Progressive dissolution of Fe_3C occurs with rising temp. H. J. E.

Diagrams for physico-chemical analysis of binary liquid systems. M. Usanovitsch (Compt. rend. Acad. Sci., U.R.S.S., 1935, **1**, 378—385).—Mathematical. W. R. A.

Viscosity of aqueous solutions. II. Mixed solutions of carbamide and urethane. A. Banchetti (Gazzetta, 1935, **65**, 159—167; cf. A., 1934, 723).—Vals. of *d* and *n* are recorded for aq. solutions of carbamide, urethane, and their mixtures (I). Vals. for (I) follow the mixture rule. O. J. W.

Viscosity and density of pure alkaline solutions and their mixtures. L. B. Hitchcock and J. S. McIlhenny (Ind. Eng. Chem., 1935, **27**, 461—466).—η and d for solutions of NaOH, Na_2CO_3, KOH, K_2CO_3, and of mixtures of the first and last two have been determined at 20°, 30°, and 40° for concns. up to 8*N*, the Ostwald–Fenske viscosimeter being used. For the mixtures η shows a deviation of −10% from that given by the additive rule. C. I.

Vapour pressure of phosphoric acid solutions. I. A. Kablukov and K. I. Zagvozdkin (Trans. Sci. Inst. Fertilisers U.S.S.R., 1933, No. 110, 4—11).—Data for aq. H_3PO_4 (5·67—87·11%) at 25°, 40°, 60°, and 80° are recorded. Ch. Abs. (*e*)

Vapour pressures of aqueous solutions. L. Frank (Z. Physik, 1935, **94**, 408—410).—Dühring's rule is used to calculate the v.p. of conc. solutions of NaCl, KCl, $CaCl_2$, KBr, $MgSO_4$, $CuSO_4$, KI, $ZnSO_4$, LiCl, and sucrose. A. B. D. C.

Mixtures of deuterium and protium oxides as ideal solutions. W. F. K. Wynne-Jones (J. Chem. Physics, 1935, **3**, 197).—Determination of the composition of the vapour for mixtures of H_2O and D_2O of known composition shows that such mixtures can be regarded as ideal solutions. N. M. B.

Association and molecular polarisation. C. Hennings (Z. physikal. Chem., 1935, **B**, **28**, 267—289).—The orientation polarisation curves of several aliphatic alcohols in C_6H_6 and C_6H_{14} solutions of molar fractions 0·01—1 have been determined at 7° and 30°. With increasing concn. each curve in general passes through a min., then through a max. The effect of rise of temp. on the form of the curves is due principally to de-association; the decrease in orientation due to increasing vigour of the mol. motions plays only a subsidiary part. C_6H_6 has a more powerful de-associating action than C_6H_{14}, but this action is less pronounced towards complexes with a finite dipole moment than towards those with zero moment. With increasing chain length the alkyl group in the single mol. becomes more and more mobile, and is thus able to protect the OH group against association. Steric hindrance also opposes association. The rise in d of the solute with increasing concn. is most rapid when association to dipole-free double mols. is occurring, but continues during association to larger complexes. F.-p. measurements show rapid increase in mol. wt. with concn. The dipole moments of $Pr^{\beta}OH$ and $Bu^{\gamma}OH$ are $1·63\pm0·02$ and $1·55\pm0·02\times10^{-18}$ e.s.u., respectively. R. C.

Optical investigation of system aldehyde–alcohol in indifferent solvents. O. Grabowsky and W. Herold (Z. physikal. Chem., 1935, **B**, **28**, 290—302; cf. A., 1933, 1036).—Absorption measurements have been made. The reaction of EtOH with CCl_3·CHO is the slower the more polar and polarisable is the solvent. With straight-chain alcohols the change from a non-polar to a polar solvent increases the shielding and saturation of the OH groups < for branched-chain alcohols. At 0° an association product of alcohol and semi-acetal in equimol. proportions seems to exist. This must lower the equilibrium aldehyde concn., but is unstable at higher temp. For reaction of EtCHO in Et_2O solution the shielding of the OH of the alcohol influences both the reactivity and the shift of the absorption max. of the EtCHO caused by the alcohol similarly, whereas in C_6H_{14} solution it affects the reactivity > the absorption shift. R. C.

Molar polarisations in extremely dilute solutions. Dipole moments of *d*-limonene, *d*-pinene, methyl benzoate, and ethyl benzoate. W. J. Svirbely, J. E. Ablard, and J. C. Warner (J. Amer. Chem. Soc., 1935, **57**, 652—655).—Dielectric consts. and d of C_6H_6 solutions of the above substances have been determined. E. S. H.

Multivalent amino-acids and peptides. III. Dielectric constants and electrostriction of the solvent in solutions of tetrapoles. J. P. Greenstein, J. Wyman, jun., and E. J. Cohn (J. Amer. Chem. Soc., 1935, **57**, 637—642; cf. A., 1934, 475).—Mols. having two NH_3^+ and two CO_2^- groups in the isoelectric condition have been studied. Diaminodithiodihexoic acid is composed of two mols. of ε-aminohexoic acid combined at the α-C atoms by S. Electrostatic attraction causes the chains to twist, and results in a relatively small effect on the dielectric consts. of solutions and on electrostriction of the solvent. Lysylglutamic acid is composed of a small dipole, glycylglycine, and a longer one between the ε-NH_2 of lysine and the γ-CO_2H of glutamic acid. Electrostatic repulsion results in a rod-shaped mol. in which the charged groups are widely separated, and the influences on increase of the dielectric const. of the solution and on the electrostriction of the solvent are maximal. E. S. H.

Relation between the structure of hydrocarbons and their miscibility with selective solvents. S. P. Mulliken and R. L. Wakeman (Rec. trav. chim., 1935, **54**, 366—372).—Miscibility of hydrocarbons has been studied with nitromethane (*a*) and less fully with Et_2SO_4 and NH_2Ph (*b*) and CH_2Ph·OH (*c*). (*a*) For liquid hydrocarbons with an equal no. of C atoms the more saturated is the less miscible. Alkanes, *cyclo*alkanes, *dicyclo*alkanes, alkenes, *cyclo*alkenes, and alkadienes with > 8 C are miscible at 20°. Alkines with C:C near the end of the chain are more sol. than alkadienes of the same mol. wt., and the temp. (T), at which demixing first appears on cooling a homogeneous mixture, rises as C:C moves to the centre of the mol. Aromatic hydrocarbons are more sol. than other types of the same mol. wt.; all are sol. below 55° and the lower ones below 20°. With solids, aromatic are more sol. than non-aromatic hydrocarbons of the same mol. wt. (*b*) Miscibility increases with unsaturation. $T_b<T_a$ and T for alkadienes and alkines is < for alkenes of the same mol. wt. (*c*) Alkanes are immiscible at temp. at which *cyclo*alkanes of the same mol. wt. are miscible. An unknown non-acetylenic hydrocarbon can be tested for aromatic character by its miscibility (*a*) at 20° for b.p. 110—220°, and at 55° for b.p. 220—300°, aromatic compounds being miscible. With an unsaturated non-aromatic acyclic hydrocarbon the presence of C:C or of a higher degree of unsaturation can be shown by the miscibility with NH_2Ph, the temp. depending on the b.p. Whether a

saturated non-aromatic hydrocarbon is cyclic or acyclic can be tested with $CH_2Ph{\cdot}OH$ at 50°, cyclic compounds being miscible. R. S. B.

Diffusion of volatile materials into an inert gas stream. E. PRESTON (Trans. Faraday Soc., 1935, **31**, 776—785; cf. A., 1933, 1242).—Further evidence is advanced for the view that evaporation proceeds from a " super surface " layer in equilibrium with the liquid phase in accordance with the Herz–Knudsen equation, and that its removal is governed by gaseous diffusion into the surrounding atm. F. L. U.

Equilibrium for gaseous and liquid phases of oxygen–nitrogen mixtures. O. N. TRAPEZINIKOVA and L. V. SHUBNIKOV (J. Tech. Phys. U.S.S.R., 1934, **5**, 949—953).—Data in presence and absence of a magnetic field are recorded. CH. ABS. (*e*)

Vapour pressure of the binary systems acetaldehyde–water and –acetic acid. N. M. MOROZOV, M. J. KAGAN, and E. S. GROSBLAT (J. Gen. Chem. Russ., 1934, **4**, 1322—1326).—The v.p.–composition curves at 10° and 20° have been determined. R. T.

Ethyl alcohol–halogen compound azeotropic couples under normal pressure. M. LECAT (Ann. Soc. Sci. Bruxelles, 1935, **55**, B, 43—47).—The formula for the azeotropic lowering (cf. A., 1927, 405) is shown to be in agreement with further experimental results. R. S.

Heterogeneous binary systems. Physical properties of systems of two liquid phases. III. H. SCHLEGEL (J. Chim. phys., 1935, **32**, 215—234).—V.p., b.p., condensation, sp. heat, mutual solubility, electrical conductivity, and heat of mixing data have been obtained for the system NH_2Ph–*cyclo*hexane. D. R. D.

Complex compounds of silver halides with halides and silver salts. S. V. GORBATSCHEV (J. Gen. Chem. Russ., 1934, **4**, 1327—1337).—The solubility of AgX in aq. NaX (X=Cl, Br, I) and aq. $AgNO_3$ has been determined; the differences between the vals. found and those calc. suggest formation of complex salts, the nature of which is discussed. R. T.

Molecular solubility of one-third basic aluminium acetate. C. ROHMANN (Pharm. Ztg., 1935, **80**, 493—495).—A review of published data supports the author's views (A., 1933, 569) rather than the theory that so-called basic Al acetate solutions are sols of $Al(OH)_3$ peptised by AcOH. D. R. D.

Solubilities of some strychnine benzoates. C. F. POE, J. F. SUCHY, and G. L. BAKER (J. Physical Chem., 1935, **39**, 239—241).—The solubilities of 27 salts of BzOH and substituted BzOH have been determined at 20—95°. M. S. B.

Solubilities of certain amino-acids and related compounds in water, densities of their solutions at 25°, and calculated heats of solution and partial molar volumes. II. J. B. DALTON and C. L. A. SCHMIDT (J. Biol. Chem., 1935, **109**, 241—248).—Solubility data are recorded for *l*-asparagine, *l*-cystine, *d*-*iso*leucine, *dl*-methionine, *l*-phenylalanine, *dl*-serine, taurine, and *l*-tryptophan. Heats of dissolution and mol. vols. are calc. and it is suggested that *dl*-*iso*leucine and *dl*-phenylalanine are *r*-compounds. H. T.

Effect of polarity on the solubilities of some organic acids. P. G. DESAI and A. M. PATEL (J. Indian Chem. Soc., 1935, **12**, 131—136).—The solubilities of BzOH (I), $CHPh{:}CH{\cdot}CO_2H$ (II), o-$OH{\cdot}C_6H_4{\cdot}CO_2H$ (III), $C_6H_4(CO_2H)_2$ (IV), and $(CH_2{\cdot}CO_2H)_2$ (V), which stand in increasing order of polarity, have been determined in 14 solvents of varying polarity. In slightly polar solvents the solubilities decrease with increasing polarity of the solute, the solubilities of (IV) and (V) being negligible. Solubility increases with polarity in the aromatic hydrocarbons, C_6H_{12}, and CCl_4, but the order is not well defined for more polar substances. $CHCl_3$ behaves abnormally with all solutes, and $COMe_2$ and $Bu^{\alpha}OH$ are abnormal in some cases. (I), (II), and (III) probably form easily dissociable solvates with alcohols, whilst (IV) and (V) form hydrates with H_2O. M. S. B.

Physical chemistry of amino-acids, peptides, and related substances. III. Solubility of derivatives of the amino-acids in alcohol–water mixtures. T. L. MCMEEKIN, E. J. COHN, and J. H. WEARE (J. Amer. Chem. Soc., 1935, **57**, 626—633; cf. this vol., 26).—A study of certain derivatives of NH_2-acids which are not zwitterions shows that the m.p. are <, and the apparent mol. vols. >, those of the NH_2-acids. The ratio of the solubility in EtOH to that in H_2O is increased approx. 3-fold for each terminal CH_2 in the mol. A CH_2 placed between strongly polar groups does not appreciably affect the solubility ratio. The solubility of NH_2-acids in EtOH–H_2O mixtures varies in the same way as salts, whereas the solubility of the derivatives varies as other uncharged org. mols. E. S. H.

Distribution of saturated monobasic aliphatic acids between water and *o*-nitrotoluene. N. A. DE KOLOSOVSKI and F. S. KULIKOV (J. Gen. Chem. Russ., 1934, **4**, 1370—1377).—Data are given for HCO_2H, AcOH, $EtCO_2H$, $PrCO_2H$, $Bu^{\beta}CO_2H$, $CH_2Cl{\cdot}CO_2H$, $CHCl_2{\cdot}CO_2H$, and $CCl_3{\cdot}CO_2H$ at 25°. R. T.

Partition of tri- and tetra-methylglucoses between chloroform and water. J. Y. MACDONALD (J. Amer. Chem. Soc., 1935, **57**, 771—772).—Partition coeffs. between H_2O and $CHCl_3$ are recorded for di- (I) and tri-methylmethylglucosides (II), tri- and tetra-methylglucose. Results obtained for the separation of (I) and (II) by partition confirm Irvine's conclusions relative to the methylation of sucrose. R. S. C.

Partition coefficient of acetone between neutral glycerides or their fatty acids and water. Influence of the alcoholic function of ricinoleic acid. A. LINDENBERG (Compt. rend. Soc. Biol., 1935, **118**, 1086—1087).—The partition coeffs. are all approx.= 0·2 except for castor oil, triricinolein, and ricinoleic acid, when the vals. are 0·25—0·30, 0·35—0·40, and 0·35—0·38, respectively. In this respect $COMe_2$ resembles EtOH and MeOH. F. O. H.

Partition coefficient between oil and water of substances completely miscible in the two solvents. I. Methyl alcohol and acetic acid in

the system castor oil–water. II. Methyl alcohol, ethyl alcohol, and acetic acid in the system triricinolein–water. A. LINDENBERG (Compt. rend. Soc. Biol., 1935, **118**, 441—444, 444—445).—I. Although MeOH and AcOH are miscible in all proportions with castor oil (I) and H_2O, their partition coeffs. in a (I)–H_2O system are different, being 0·12 and 0·2—0·24.

II. The partition coeffs. of MeOH, EtOH, and AcOH for the system triricinolein–H_2O are the same, viz., 0·23 at 20°. A. L.

Physical chemistry of amino-acids, peptides, and related substances. IV. Distribution coefficients of amino-acids between water and butyl alcohol. A. ENGLAND, jun., and E. J. COHN (J. Amer. Chem. Soc., 1935, **57**, 634—637; cf. this vol., 695).—Distribution coeffs. have been determined at 25°. As the length of the hydrocarbon chain increases the concn. in the aq. phase is less and that in the BuOH phase greater. NH_2-acids with branched chains behave like smaller mols. BuOH and NH_2-acids reciprocally diminish the solubility of the other in H_2O. E. S. H.

Gas adsorption and Nernst's heat law. M. TEMKIN (Acta Physicochim. U.R.S.S., 1934, **1**, 36—52).—On the basis of Langmuir's conception of adsorption, the adsorption equation is deduced thermodynamically. The adsorption equilibrium is determined by the vals. of the heat of reaction, the mol. heat, and the chemical const. The application of Nernst's approximation formula to the determination of the velocity of evaporation of O atoms from a W surface, the oxidation velocity of W, the velocity of evaporation of Th from a W surface, the time required for the adsorption of A on glass, and the evaluation of the heat of adsorption, gives vals. in good agreement with the results of experiment. The possibility of determining the true heat of activation in heterogeneous catalysis, and hence the equilibrium requirements and the mechanism of reaction, is discussed. M. S. B.

Heterogeneous catalysis. I. Activated adsorption of hydrogen on carbon. E. STORFER (Z. Elektrochem., 1935, **41**, 198—204).—The adsorption of H_2 on active C containing 1% of Ni has been measured at 155° and 206° and at pressures < 8 mm. Hg. Energies of activation are calc. F. L. U.

State of the sorbed phase. I. Sorption velocity measurements with methane, ethane, and propane on activated carbon. E. BERL and E. WEINGAERTNER (Z. physikal. Chem., 1935, **173**, 35—57).—Measurements have been made at 0—261° and 10^{-4}—1 cm. Above the crit. temp., T_c, in the linear region of the sorption Langmuir's velocity equation (I) is valid. Below T_c for C_2H_6 and C_3H_8 the velocity curves show that equilibrium is attained by at least two consecutive processes, for each of which (I) holds. These are taken to be sorption of the gas and two-dimensional condensation to liquid of the sorbed phase. The rate of establishment of equilibrium is a min. at T_c. Above T_c the variation of sorption velocity with temp. may be represented by an Arrhenius function, the energy of activation deduced from which, E, must be regarded as the energy barrier between the sorption space and the extended phase when a mol. approaches the surface. For a given C, E is the same for all three gases, showing that sorption must occur at the Me group, *i.e.*, the sorbed C_2H_6 and C_3H_8 mols. must have their axes perpendicular to the surface. R. C.

Heats of adsorption of certain organic vapours on activated charcoal at 25° and 50°. J. N. PEARCE and G. H. REED (J. Physical Chem., 1935, **39**, 293—301).—Heats of adsorption (I) of MeCl, $Pr^{\beta}Cl$, $Bu^{\alpha}Cl$, $Bu^{\beta}Cl$, and $Bu^{\gamma}Cl$ on C have been measured at 25° and 50°, and of EtCl and $Pr^{\alpha}Cl$ at 50°. The temp. coeff. is practically negligible. (I) increase with length of chain and for straight-chain compounds are > for branched. Total (I) for any vapour increase rectilinearly with the total amount adsorbed. M. S. B.

Sorption of halogens by silica gel and charcoal. L. H. REYERSON and A. E. CAMERON (J. Physical Chem., 1935, **39**, 181—190; cf. following abstract).—On coconut C the rate of sorption of Br and I is < on SiO_2 gel and it is impossible to remove all the Br by desorption. The type of isotherm obtained is quite different from those for SiO_2; it indicates the formation of a unimol. layer of adsorbed mols. followed at higher pressures by diffusion into the C. M. S. B.

Sorption of bromine and iodine by silica gel. A. E. CAMERON and L. H. REYERSON (J. Physical Chem., 1935, **39**, 169—179).—The sorption of Br by SiO_2 gel at 58°, 79°, 117·5°, and 137·7°, and that of I at 98·2°, 137·6°, 158·3°, 178·4°, and 198·5° has been determined using a McBain and Bakr sorption balance with a quartz spiral manometer. Adsorption and desorption are completely reversible. The curves for Br at higher temp. are practically linear; the rest are convex towards the pressure axis, indicating weak binding forces and physical adsorption. The adsorption of Br is much > that of I. The data do not fit the classical adsorption isotherm. M. S. B.

Adsorption from solution. III. Adsorption of picric acid by silica gel. L. S. TS'AI and T. S. LO (J. Chinese Chem. Soc., 1935, **3**, 16—21).—The adsorption of picric acid from aq. solution by SiO_2 gel at 25° follows the Langmuir equation and is mainly a continuous process. The results may be explained by the presence of a H_2O envelope on the surface of the SiO_2. J. W. S.

Density and adsorption studies in the region of the critical temperature: system dimethyl ether–alumina. J. EDWARDS and O. MAASS (Canad. J. Res., 1935, **12**, 357—371; cf. A., 1933, 1241).—A method is described for the simultaneous measurement of d and the adsorption of liquids, vapours, and gases near the crit. temp. (T_c). The adsorption of liquid Me_2O on Al_2O_3 begins only at 124°, but increases with temp. to a max., beyond which it follows the form of a normal isobar. The discontinuities observed in the adsorption cannot be attributed to changes in the d of the adsorbed phase or to persistence of liquid in the pores of the Al_2O_3 above T_c, and there is no evidence for the existence of a lag in T_c. As a d hysteresis is found up to 14° above T_c, the effects

are ascribed to the persistence of liquid-like structure in the gas. Irregularities in d are also observed below T_c. J. W. S.

Adsorption and hydrolysis of adsorbed glycogen. S. Simonovits (Biochem. Z., 1935, **277**, 72—76).—In their experiments with glycogen (I)–animal charcoal (II)–HCl and (I)–(II)–amylase, Bancroft and Fry (A., 1933, 457) overlook the fact that the product of hydrolysis of (I), viz., glucose (III), is itself adsorbed by (II). Adsorption of (I) by (II) is irreversible (difference from mechanical adsorption), and leads to no true equilibrium, and the adsorbed (I) is not eluted by AcOH, HCl, or (III). Hydrolysis of (I) at the (II) surface is complete. P. W. C.

Adsorption and ion exchange. A. H. W. Aten, jun. (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 441—449).—Theoretical. Langmuir's formula is modified to allow for the influence of adsorbed mols. on the adsorption heat (E), which is given by $E=E_0+ga$, where g is a const. and a is the amount adsorbed. The formula $a/p=k_1a_{\max.}e^{-a/a_{\max.}+ga/RT}$ (I) is deduced (p=gas pressure, k_1=const.) and is analogous to the formulæ of Schmidt, Williams, and Henry. (I) is applied to the exchange of ions in permutite, giving $\log x_Ac_B/x_Bc_A=k_2x_A+k_3$ (II), where x_A and x_B are the amounts of exchangeable ions on the surface, and c_A and c_B are their aq. concns., k_2 and k_3 being consts. The results of Rothmund and Kornfeld (A., 1918, ii, 315) agree with (II). R. S. B.

Sorption of basic dyes on Cellophane. N. Andô (J. Chem. Soc. Japan, 1934, **55**, 959—967).—The adsorption of methylene-blue by Cellophane follows Freundlich's equation. Ch. Abs. (*e*)

Adsorption of optical sensitisers for silver salts. A. I. Rabinovitsch, J. I. Bokinnik, and T. B. Ridiger (Kino-Photo Inst. Moscow, 1934, **2**, 161—165).—A method is given for measuring the partition coeff. of the dyes between solution and AgBr. The adsorption is lowered by Br′.

Ch. Abs. (*e*)

Adsorption at crystal–solution interfaces. VII. Effect of stirring and growth rates on the habit and dye adsorption of alum crystals. Influence of acid and alkali media on the habit of alum crystals. (Miss) P. A. Paine and W. G. France (J. Physical Chem., 1935, **39**, 425—429).—Stirring causes a decrease in the size of the cube faces of K alum crystals grown from pure solutions or aq. Diamine Sky Blue of varying concn. From the same concn. of dye less colour is adsorbed by crystals from stirred than from unstirred solutions, or when prepared by rapid cooling than by slow evaporation at room temp. An explanation based on rate of diffusion of ions is discussed. No appreciable change of habit occurs when alum crystals are grown from acid solutions or from solutions containing Na_2CO_3 from which $Al(OH)_3$ is not pptd. M. S. B.

Copper sulphide–water contact angles. C. C. de Witt (J. Amer. Chem. Soc., 1935, **57**, 775—776).—The contact angle is due to the presence of an adsorbed air film. E. S. H.

Surface friction and adsorption on metals. P. Rehbinder, N. Kalinovskaja, and H. Michallova (Acta Physicochim. U.R.S.S., 1934, **1**, 22—26).—Measurements have been made of the "lubricability," or diminution in the coeff. of friction, of Cu, alloys of Cu and Al, Al, Mg, and Sn by the pure media H_2O and vaseline oil, and by solutions in these of surface active materials such as p-$C_6H_4Me{\cdot}NH_2$ (I) and NH_2Ph. (I) increases the coeff. of friction on Al and decreases it on Cu; it must therefore be oppositely oriented on the two surfaces. M. S. B.

Surface tension of homologous series. J. H. C. Merckel (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 387—393).—For solutions of straight-chain acids, esters, and alcohols σ varies linearly with c (mol. per litre) up to a definite concn., and in this range log tan θ, where θ is the angle made by the σ–c line with the c axis, varies linearly with the no. (n) of C atoms in the series (n, 1—6). The plots of log tan θ against n are parallel for different types, and isomerides give identical points. At higher concns. for solutions of fixed concn. $\sigma=al^2+bl+c$, where a, b, and c are consts., and l=length of C chain. With Na salts of the fatty acids (n=2—14), log tan θ is a quadratic function of n. Szyskowski's representation of capillary phenomena is criticised. R. S. B.

Investigation of adsorbed films by means of a photo-electric counter. C. Ouellet and E. K. Rideal (J. Chem. Physics, 1935, **3**, 150—158).—A high-sensitivity tube counter of special design has been used to measure the changes in the work function ϕ of Au due to adsorbed layers. Accurate determinations of thresholds (T) can be made with continuous ultra-violet light of moderate intensity, and the quant. variation of ϕ with the amount of adsorbed material can be followed continuously. ϕ for strongly oxidised and strongly reduced Au differs by 1·58 volts; the oxidation shows two definite stages with respective increases in ϕ of 0·35 and 0·70 volt. The adsorption of I vapour is reversible and the resulting increase in ϕ varies with the I pressure according to a Langmuir isotherm, $\Delta\phi$ at saturation being +0·21 volt. The adsorption of EtOH on Au is reversible and gives rise to a double T consisting of the original Au T and a new T corresponding with a decrease of 0·49 volt in ϕ, this val. being independent of the EtOH pressure. The intensity of emission at the new T increases with the pressure, indicating that the EtOH is condensed as a two-dimensional liquid covering an area which increases with pressure. N. M. B.

Formation of multimolecular layers at the surface of separation between mercury and solution. A. Frumkin, A. Gorodetzkaja, and P. Tschugunov (Acta Physicochim. U.R.S.S., 1934, **1**, 12—21).—Using the capillary electrometer it is shown that hexoic acid and PhOH are adsorbed as a multimol. layer at the surface of separation between Hg and aq. solution, contrary to the behaviour at a solution–air surface of separation. Since the thickening takes place without any abrupt change of potential, it is suggested that the hexoic acid layer must be $\lesssim$ 3 mols. thick, additions to the unimol. layer being made by double mols. in which the dipoles of the separate mols. counteract each other. M. S. B.

Surface pressures and potentials of unimolecular films of long molecules: polymerides of ω-hydroxydecoic acid. W. D. HARKINS, H. E. RIES, jun., and E. F. CARMAN (J. Amer. Chem. Soc., 1935, **57**, 776—777).—The data show that the mols. lie flat on the surface, anchored by the polar groups at the ends and at every tenth C; they may have as many as 149 regions of attachment. E. S. H.

Surface potentials of aqueous solutions of octyl alcohol and octoic acid. I. SAWAI (Trans. Faraday Soc., 1935, **31**, 765—769).—The surface potentials for both substances, measured by means of an air electrode coated with Po, increase with concn., and with decreasing p_H. The results are discussed. F. L. U.

Surface potentials of alkaloid solutions. B. KAMIENSKI (Bull. Acad. Polonaise, 1934, **A**, 391—393).—Aq. solution–air potentials ranging from 0 to 442 mv. have been observed with solutions of quinine, cinchonidine, cinchonine, strychnine, brucine, pilocarpine, atropine, amarine, morphine, codeine, veratrine, caffeine, and theobromine and their salts. J. G. A. G.

Electrokinetic properties of proteins. III. Rôle of electrical forces in the adsorption of gliadin at a glass–liquid interface. W. McK. MARTIN (J. Physical Chem., 1935, **39**, 249—263).—A study of streaming potentials at a glass surface, in solutions of gliadin (I) of varying p_H, indicates that (I) is adsorbed from solutions in which it is positively charged, glass being always negative, but reversal of the charge of (I) to negative does not result in complete desorption. A highly purified solution of (I) is not chemically homogeneous, but contains within the isoelectric range both positively and negatively charged fractions. When (I) is adsorbed on glass free $\cdot NH_2$ and $\cdot CO_2H$ are turned towards the liquid phase; these react with acids and alkalis, respectively, within the p_H range 4·88—8·83. The true isoelectric range of a protein is probably identical with the "p_H stability region." M. S. B.

Linear phenomena. III. Linear adsorption and gelatinisation of lyophilic systems. D. TALMUD (Acta Physicochim. U.R.S.S., 1934, **1**, 145—159).—The spontaneous formation of colloidal skins at the surface of solutions of half-colloids may be observed ultramicroscopically. It is suggested that this may be due to linear adsorption at the junction of the two phases of the solution with a third phase such as a gas at the surface or the wall of the containing vessel. The colloidal skin may be obtained artificially by the addition of insol. linear active materials, *e.g.*, cetyl alcohol to saponin solutions. By repeatedly removing the skin, which may be regarded as due to two-dimensional gelatinisation, the whole solution may ultimately be gelatinised. A no. of phenomena, hitherto inexplicable, are probably due to linear adsorption. The connexion between linear adsorption and emulsification in the absence of emulsifiers, especially in solutions containing gases, is discussed. The application of linear adsorption to the stabilisation of foams has been demonstrated experimentally. M. S. B.

Theory of electrocapillarity. III. S. R. CRAXFORD, O. GATTY, and J. ST. L. PHILPOT (Phil. Mag., 1935, [vii], **19**, 965—989; cf. A., 1934, 140).—The theory of electrocapillarity is considered in relation to a generalised mechanism in which only external work terms are involved, and a general equation derived which includes those of Lippmann and Gibbs as special cases. R. S.

New electrocapillary effect. N. BACH (Acta Physicochim. U.R.S.S., 1934, **1**, 27—35).—When drops of Hg fall through a solution of a Hg^I salt and an indifferent electrolyte, such as KNO_3, a current of electricity flows through the solution in the same direction as the current produced by electrokinetic effects and > the latter. It is caused by the deformation of the Hg drops by the action of the induced surface charges. For a given concn. of Hg^I salt the current intensity increases with increasing total concn. of electrolyte; the electrokinetic current shows the contrary behaviour. By reducing the diameter of the Hg drops the electrocapillary effect is decreased, but it is improbable that the electrokinetic effect ever preponderates. M. S. B.

Rôle of evaporation in the phenomenon of imbibition by porous bodies. (MLLE.) P. BERTHIER (Compt. rend., 1935, **200**, 1105—1107).—In an atm. saturated with H_2O vapour pure H_2O rises more rapidly than a solution in a strip of porous paper, the rate being least in the more viscous solutions, but in an atm. dried with $CaCl_2$ or other drying agent the rate of rise increases with concn. This behaviour is due to the greater rate of evaporation from the dil. solution in the porous support than from the conc. in a dry atm. M. S. B.

Electrokinetic potentials. I. Measurements at the interfaces between fibres and water. N. ANDÔ and A. ANDÔ (J. Chem. Soc. Japan, 1934, **55**, 968—978).—Electrokinetic potentials of cotton, silk, and wool have been measured by the streaming-potential method. They are negative. CH. ABS. (*e*)

Factors influencing the cataphoresis of small particles in water. C. L. S. GILFORD (Phil. Mag., 1935, [vii], **19**, 853—878).—The dependence of cataphoretic velocity (I) on the form of apparatus, temp., and the diameter, conductivity, and shape of particle has been examined. (I) vals. are given for graphite, sugar C, Sb, Sb_2S_3, and MnO_2 in H_2O of different conductivities. The results are discussed in relation to current theories. R. S.

Electrophoresis of artificial calcium–carbamic acid complexes. G. PERETTI (Boll. Soc. ital. Biol. sperim., 1934, **9**, 1329—1330).—Ca transport is cathodic in complexes derived from glycine, carbamide, or NH_3, which are therefore not responsible for the anodic Ca transport in the electrophoresis of serum. R. N. C.

Electrodialysis of artificial systems of calcium chloride and alkali citrates. G. PERETTI (Boll. Soc. ital. Biol. sperim., 1934, **9**, 1331—1333).—Addition of citrate to $CaCl_2$ solutions renders Ca transport anodic with small currents and cathodic with large

currents; Ca thus associates with citrates in such a system in a non-ionisable form. R. N. C.

Concentration changes at membranes and the electro-osmotic membrane potentials. J. J. Bikerman (J. Physical Chem., 1935, **39**, 243—247).—From the theory of the diffuse double layer the concn. changes and potential differences at diaphragms through which an electro-osmotic current is driven have been derived and compared with experimental results. M. S. B.

"Diffusion effect" on ionic distribution. I. Theoretical considerations. T. Teorell (Proc. Nat. Acad. Sci., 1935, **21**, 152—161).—In an aq. system of strong electrolytes, characterised by a steady diffusion across an ion-permeable boundary (membrane), theoretical considerations predict (*a*) the possibility of development of concn. differences of "passive" ions ("diffusion effect" on ionic distribution), and (*b*) an approach to a steady state of the system as a whole, where the "passive" ions are in a true state of equilibrium. The "diffusion effect" appears when a concn. gradient is present and is due to differences in ionic mobility (relative impermeability), whereas the "Donnan effect" is caused by abs. impermeability of one or several ion species. Diffusion effects of the type discussed may be of biological importance. O. J. W.

Influence of the presence of a solute on the rate of osmosis. R. N. Traxler and H. N. Huntzicker (J. Physical Chem., 1935, **39**, 431—435).—In the osmotic system C_5H_5N–rubber–H_2O, examined at 35°, the rate of osmosis of C_5H_5N into H_2O is retarded by solutes in either liquid, as shown by the effect of dissolving anthracene or $AgNO_3$ in C_5H_5N and sucrose or KCl in H_2O. Dissolved or dispersed rubber in C_5H_5N has also a marked retarding effect. M. S. B.

***tert.*-Butyl alcohol as a solvent for cryoscopic mol.-wt. determinations.** G. S. Parks, G. E. Warren, and E. S. Greene (J. Amer. Chem. Soc., 1935, **57**, 616—619).—Determinations of the mol. wt. of 28 org. compounds show that $Bu^{\gamma}OH$ is a suitable solvent for most org. compounds, including primary alcohols and all classes of hydrocarbons. It is unsuitable for certain closely related *sec.*- and *tert.*-alcohols, owing to the formation of mixed crystals on freezing. The cryoscopic const. is 8·25. E. S. H.

Osmotic behaviour of solutes as a function of the specific interaction between solvent and solute. K. Fredenhagen (Physikal. Z., 1935, **36**, 321—335).—The lowering of v.p. is a consequence of the sp. interaction between solute and solvent in accordance with stoicheiometric relations or those described by the term solvation. Only the former type is compatible with Raoult's law. The behaviour of polar solvents and solutes with respect to association (I) is discussed. When the mols. of the solvent possess a single polar group (II), the solute occurs in single mols. except where it is associated in the vapour phase. When the mols. of the solvent have more than one (II), the formation of solvates is possible. Introduction of (II) into the solvent mol. opposes (I) of the solute, but in the solute it aids (I). A. J. M.

Dielectric constant of electrolytes. R. W. McKay (Canad. J. Res., 1935, **12**, 377—397).—Bridge and voltage-resonance methods of measurement are described and discussed. Aq. solutions of NaCl, HCl, K_2SO_4, $MgSO_4$, $CuSO_4$, and $K_4Fe(CN)_6$ at 23° and at 2×10^6 cycles show an increase in ϵ with concn. > that predicted by Debye and Falkenhagen (A., 1928, 957). The results are in approx. accord with those of Lattey and Davies (A., 1932, 120, 224). J. W. S.

Saturation effect of dielectric constants of solutions of electrolytes. W. Hackel (Physikal. Z., 1935, **36**, 220—222).—The saturation effect for $1—2 \times 10^{-3}$ molar solutions of LiF and KCl is $< 0{\cdot}1\%$. The difference between the effect for LiF and KCl is $< 0{\cdot}05\%$. A. J. M.

Electrical excitation in electrolytes. M. Planck (Z. Physik, 1935, **94**, 469—472).—When ionic concns. can be assumed const., space-charge effects do not give appreciable differences in the over-all concns. of oppositely-charged ions. A. B. D. C.

Dielectric constants of solutions of amphoteric electrolytes. II. O. Blüh and J. Kroczek (Z. physikal. Chem., 1935, **B**, **28**, 410; cf. this vol., 166).—A correction. R. C.

Observation of the Brownian movement with the unaided eye. J. Obrist (Physikal. Z., 1935, **36**, 343—344).—Observations similar to those of Andreev (A., 1934, 361) were made in 1907 by Molisch, with the sap of spurge. Andreev's conclusions are criticised, and those of Lau and Johannesson (this vol., 162) confirmed. Conditions are described for observation of the Brownian movement in mastic sols with the unaided eye. A. J. M.

Observation of the Brownian movement with the unaided eye. J. Schintlmeister (Physikal. Z., 1935, **36**, 345).—Attention is directed to the work of Molisch (see preceding abstract). A. J. M.

Sedimentation velocity and sediment volumes of native potato starch with variation of hydrogen-ion concentration. E. Wiegel [with H. Schüler] (Kolloid-Z., 1935, **71**, 65—73).—Sedimentation velocity (I) increases rapidly with increasing [H·] of the suspension. In general, the sediment vol. increases with decreasing (I), but passes through a max. when a certain val. is reached. The sorption of HCl by starch has been studied and is discussed in relation to the above phenomena. E. S. H.

Velocity of vaporisation of small drops in a gas. N. Fuks (Physikal. Z. Sovietunion, 1934, **6**, 224—243).—The Maxwell diffusion laws are extended to the evaporation of small drops. Ch. Abs. (*e*)

Colloidal gases. III. Colloidal air and colloidal oxygen with a bubble size of 5 mμ or 3 mμ diameter. A. Krause and K. Kapitańczyk (Kolloid-Z., 1935, **71**, 55—60; cf. A., 1934, 487).—The sols are prepared by dilution of distilled H_2O (containing dissolved air or O_2) with a large vol. of 18·55—19·60*N*-NaOH. E. S. H.

Aggregation of aërosols by sound waves. O. Brandt and H. Freund (Z. Physik, 1935, **94**, 348—355).—Micro-cinematographic records of the stages of aggregation are reproduced. A. B. D. C.

Theory of coagulation of colloids and of smokes. W. R. HARPER (Trans. Faraday Soc., 1935, **31**, 774—775).—Errors in a previous paper (A., 1934, 960) are corr. F. L. U.

Significance of gas phases in the mechanical synthesis of disperse mercury systems. (Agitation synthesis and ultrasonic-wave synthesis.) N. SATA (Kolloid-Z., 1935, **71**, 48—55).—When shaken by hand, Hg disperses to a sol in 0·001*M*-K citrate in presence of air, but not in presence of H_2, N_2, or in vac. Under the influence of ultrasonic waves, dispersion takes place in presence of any of the above gases, or in vac., but unstable emulsions are formed, containing no colloidal particles. The order of rate of sedimentation after removal of the ultrasonic wave source is vac. > H_2=N_2 > air. E. S. H.

Behaviour of high-molecular compounds in solution. R. SIGNER (Helv. Chim. Acta, 1935, **18**, 701—703).—A discussion of the discrepancy between mol. wt. determined by the ultracentrifugal and osmotic methods. E. S. H.

Behaviour of complex and very complex molecules in solution. R. SIGNER (Helv. Chim. Acta, 1935, **18**, 701—703).—Comparison of ultracentrifugal and v.-p. measurements shows that the osmotic behaviour of very long and short thread mols. is analogous. H. W.

Specific inductive capacity of colloidal solutions. J. J. BIKERMAN (J. Chim. phys., 1935, **32**, 285—292; cf. A., 1934, 162).—The high dielectric const. of sols is explained by the existence of a conducting layer between the particle and the solvent, and an equation is derived which is in accord with the experimental data. R. S.

Colloidal sulphur. Dehydration of sulphur hydrosols. I. MARKEWITSCH (Rev. Chim. ind. Quesneville, 1934, **43**, 175—178; Chem. Zentr., 1934, ii, 3736—3737).—Three types of crystal were isolated by the action of EtOH or EtOH–Et_2O on colloidal S: small rhombic crystals; long prismatic needles; and hexagonal lamellæ (m.p. 108·2°). H. J. E.

Viscosimetric investigations of structure formation in vanadium pentoxide sols. II. Influence of heating. A. RABINERSON and G. SCHUMANN (Kolloid-Z., 1935, **71**, 87—94; cf. A., 1934, 1068).—When conc. V_2O_5 sols (1—1·5%) are heated for a short time at 50—80° the viscosity (η) decreases at first and then increases to above the initial val. Prolonged boiling gives unstable η vals. and ultimately a decrease in η. The behaviour is ascribed to (*a*) dissolution of colloid particles, (*b*) destruction of the oriented structures, (*c*) acceleration of the lengthwise growth of the particles, (*d*) acceleration of unoriented coagulation. E. S. H.

Viscosimetric investigations of structure formation in $Fe(OH)_3$ sols. I. Sols containing electrolyte. A. RABINERSON (Acta Physicochim. U.R.S.S., 1934, **1**, 168—176; cf. A., 1934, 142).—The gradual peptisation of an aged $Fe(OH)_3$ gel on dilution is indicated by a decrease in viscosity with time. Discontinuities in the viscosity–time curves, in presence of K_2SO_4, indicate changes of structure through the action of the electrolyte. The thixotropic behaviour of $Fe(OH)_3$ gels has also been studied. The property may be retained by these gels for a considerable length of time. M. S. B.

Chromium hydroxide hydrosols and the Burton–Bishop rule. E. FISHER and C. H. SORUM (J. Physical Chem., 1935, **39**, 283—287).—Purified $Cr(OH)_3$ sols follow the Burton–Bishop rule (I) for all ions. After the addition of sufficient $CrCl_3$ (I) for univalent ions breaks down. On dilution with EtOH the very highly purified sols do not follow (I) for univalent ions, but (I) holds for less highly purified sols. This is probably due to the greater influence of hydration on the stability of the highly purified sols. M. S. B.

Electrochemistry of colloids. II. Electrochemical properties of TiO_2 sols. V. KARGIN (Acta Physicochim. U.R.S.S., 1934, **1**, 64—73).—Positive TiO_2 sols are prepared by pouring aq. $TiCl_4$ into H_2O and dialysing. With ice-cold H_2O a transparent hydrophilic sol is obtained. In hot H_2O the sol is milky and more hydrophobic. The former gelatinises on long dialysis. By peptising the gel with tartaric acid and dialysing a negative sol is obtained. A negative sol is also obtained by treatment of the positive sol with alkali. Potentiometric titration with salt solutions indicates that there is strong exchange adsorption of anions, but not of cations, whilst the reverse is the case with negative sols, where there is marked exchange displacement of cations including $H^{\cdot}$. By dilution of the positive sol there is no dissociation of TiO_2 into $H^{\cdot}$ and the corresponding anion, as might be expected for an amphoteric compound, and the charge remains positive. M. S. B.

Red limit of the photo-electric effect in potassium–ether sols. V. KARGIN and E. FODIMAN (Acta Physicochim. U.R.S.S., 1934, **1**, 74—78).—The external photo-electric effect of red monochromatic light on K–Et_2O sol, with and without adsorbed KI, has been studied. The adsorbed negative ions cause an increase in the photo-electric current and shift the limit of the effect towards the red end of the spectrum. After drying the sol the photo-electric current is still further increased, but the red limit is not altered, showing that the phenomena take place at the metal–solution and not at the solution–vapour interface. Hydrosols of Ag, Cu, and Bi show similar behaviour. M. S. B.

Heterogeneous chemical reactions under the silent electric discharge. XII. Preparation of colloidal solutions. II. S. MIYAMOTO (J. Chem. Soc. Japan, 1934, **55**, 1273—1276; cf. this vol., 46).—As hydrosols are formed when dil. As_2O_3 solutions are subjected to a silent electric discharge in a current of H_2. A mixture of AsH_3 and H_2 gives similar results. Alcohol sols are obtained by replacing H_2O by EtOH, $Bu^{\beta}OH$, or C_5H_{11}·OH. Sb sols are formed from dil. aq. K Sb tartrate or SbH_3+H_2 under similar conditions. Similar sols of HgCl are formed from $HgCl_2$ under the discharge. CH. ABS. (*e*)

Effect of temperature on the stability of a hydrosol of iron hydroxide in an alcohol–ether mixture. A. V. DUMANSKI and I. T. MARKEVITSCH (J. Phys. Chem. U.S.S.R., 1933, **4**, 914—917).—Data

are given for temp. from −15° to 130°. The influence of temp. is discussed. CH. ABS. (*e*)

Depth effect of orienting forces and the stability of foams and emulsions. S. E. BRESLER and D. L. TALMUD (J. Phys. Chem. U.S.S.R., 1933, **4**, 796—801).—Data are recorded for the effect of 3—25% aq. KCl, KBr, KI, K_2SO_4, $K_3Fe(CN)_6$, KCNS, and $BaCl_2$ on C_6H_6 emulsions. Quasi-crystal complexes are oriented by the effect of the boundary layer, and in such cases the hydration of polar groups must exert an additional depth effect in some sizes of complexes. CH. ABS. (*e*)

Measure for the separation of emulsions (demulsification). E. L. LEDERER (Kolloid-Z., 1935, **71**, 61—64).—The rate of separation of a phase is expressed by $dV/dt=k(1-V)V^{\frac{1}{2}}$, where V is the vol. of the liquid phases separating in the time t. E. S. H.

Viscosity and plasticity of disperse systems. III. Plastic properties of resin soaps. M. P. VOLAROVITSCH (Kolloid-Z., 1935, **71**, 22—28; cf. this vol., 444).—Two methods of determining the flow velocity (θ) of resin soaps are described. Results show that θ is a physical const., which is independent of the dimensions of the apparatus. The dependence of θ on temp. and H_2O content has been investigated. E. S. H.

Quicksand as a thixotropic system. H. FREUNDLICH and F. JULIUSBURGER (Trans. Faraday Soc., 1935, **31**, 769—774).—Samples of quicksand from the Lancashire coast have been shown to contain more fine clay than ordinary sand from the same localities. One such sample, containing 2·1% of clay, was thixotropic when mixed with sea-H_2O. The thixotropy vanished when the clay was removed by centrifuging. In all the samples examined thixotropy was associated with loose packing. F. L. U.

Dielectric investigations on dissolution, swelling, and thixotropy of cellulose triacetate in chloroform and chloroform–benzene. I. SAKURADA and S. LEE (Kolloid-Z., 1935, **71**, 94—100).—Dielectric consts. have been determined in solutions of glucose penta-acetate (I) in C_6H_6 and of (I), cellobiose octa-acetate (II), cellulose-dextrin acetate (III), and cellulose triacetate (IV) in $CHCl_3$. 1 g. of (I) binds 0·14 g. of $CHCl_3$. The polarisations of (II), (III), and (IV) are practically equal. (IV) has a dipole moment of about 2×10^{-18} e.s.u., independently of the viscosity. Either the (IV) mol. is dissolved in a low-mol. form and the mol. is free to orient itself in the electric field, or the dipole groups in the (IV) mol. are free to rotate. In the thixotropic sol–gel transformation of (III) and (IV) in C_6H_6–$CHCl_3$ the dielectric const. and polarisation remain unaltered. (III) which has swelled in C_6H_6–$CHCl_3$ also possesses orientation polarisation, but to a smaller extent than in the dissolved state. E. S. H.

Coacervate sols and their relation to the theory of lyophilic colloidal stability. H. G. B. DE JONG and P. v. D. LINDE (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 419—426).—The effect of varying the ratio EtOH/H_2O has been studied with glycogen sols. At 0—37 vol.-% of EtOH the mixtures are clear, at 37—47% strong turbidity slowly develops, at 47—80% there is opalescence increasing to turbidity with increasing concn. of EtOH, and at > 80% flocculation occurs. The opalescent mixtures (coacervate sols) behave as hydrophobic sols with a small negative charge which is unevenly distributed over the surface of a colloidal particle. The tendency towards spontaneous coacervation decreases as the charge on the particle increases. R. S. B.

Oriented coacervates and their bearing on the formation of colloid-crystals. H. G. B. DE JONG (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 426—434).—On adding 3 vols. of EtOH to 2 vols. of a 2% starch sol (Huron) and warming the resulting opalescent coacervate sol at 70° for 15 min. a platelet sol (I) is formed. Electrolytes and oleic acid impede the formation of (I). The particles of (I) carry a negative charge, have a diameter 5—6 μ, flocculate on shaking, and can also be obtained reversibly by cooling clear sol from 90°. With MeOH and $Pr^{\beta}OH$ the plates are smaller. Other preps. of amylum show a more complex but similar behaviour, all sols containing a variety of colloid fractions, some of which give ordinary and others oriented coacervates. The bearing of oriented coacervation on the formation of protein crystals is discussed. R. S. B.

Action of strong and weak bases on cellulose nitrate. II. Solvatation of the polymeric-homologous series of cellulose nitrates treated with ammonia. L. I. MIRLAS (J. Gen. Chem. Russ., 1934, **4**, 1338—1346).—According to Mark and Fickentscher's formula the sp. η should be $\propto M$ (mol. wt.), whilst according to Staudinger's formula $\eta \propto M^{0\cdot5}$. M of cellulose nitrates treated with various concns. of aq. NH_3 have been calc. from these formulæ, and the deviations compared. R. T.

(A) Effect of heat-treatment on viscosity of gluten dispersed in alkali, acid, and neutral solvents. (B) Hydrolysis of gluten induced by solvent. W. H. COOK and R. C. ROSE (Canad. J. Res., 1935, **12**, 238—247, 248—252).—(A) The decrease in η of dispersions of gluten in NaOH on heating is > in AcOH. In aq. carbamide and Na salicylate (I) heating below 70° decreases η; above 70° η passes through a max.

(B) The unimol. velocity coeff. and temp. coeff. of hydrolysis of gluten in dil. aq. NaOH are > in aq. AcOH. Gluten is not hydrolysed in aq. carbamide or (I). H. D.

Explanation of hysteresis in the hydration and dehydration of gels. J. W. MCBAIN (J. Amer. Chem. Soc., 1935, **57**, 699—700).—Hysteresis is a consequence of the v.-p. relations in capillaries. E. S. H.

Lyophilic colloids. V. Dissolution of gelatin and stability of its sols. I. N. PUTILOVA. **VI. Fractionation of gelatin and physico-chemical properties of the different fractions.** S. M. LIEPATOV and I. N. PUTILOVA (Kolloid-Z., 1935, **71**, 80—82, 83—87; cf. A., 1934, 1306).—V. By fractionation of gelatin by dissolution in H_2O, and studies of the influence of the fractions on the rate of gelation and the rate of coagulation by EtOH, it is shown that the solubility and stability of gelatin depend on the concn. of the fractions of low mol. wt.

VI. The mol. wt., solvation no., and length of principal valency chains have been determined for different fractions of gelatin obtained by selective dissolution in H_2O. There is no evidence of the existence of different chemical species in the fractions. E. S. H.

Existence of different forms of gelatin. N. Peskov and N. Zürupa (Kolloid-Z., 1935, **71**, 73—79).—Experiments on dissolution in H_2O, adsorption by kaolin, and salting-out by $(NH_4)_2SO_4$ show the existence of five forms of gelatin, three of which have peptising properties. The changes occurring on ageing are discussed. E. S. H.

Reaction of silver ions with gelatin. P. Wulff and W. Ehrenberg (Phot. Korr., 1934, **70**, 155; Chem. Zentr., 1934, ii, 3891).—From conductivity and transport measurements it is shown that $Ag^{\cdot}$ forms a complex anion with gelatin of the type $\{[Ag^{\cdot}(Gel.^{-})_2]^{-}\}_n$. The solubility of AgCl may be increased to 100 times its normal val. in H_2O by the presence of gelatin. H. J. E.

Reaction of silver ions with gelatin. P. Wulff (Z. wiss. Phot., 1935, **34**, 59—62; see preceding abstract).—Conductivity measurements show that [Cl′] is reduced by gelatin; the increased solubility of AgCl in gelatin is therefore not due to the Cl′. It is probable that about half the Ag^+ is free and the rest bound. Conductivities of various AgCl, Ag_2O, and NaCl solutions in gelatin have been determined. J. L.

Diffusion coefficients of molecules and ions from measurements of undisturbed diffusion in a stationary medium. W. G. Eversole and E. W. Doughty (J. Physical Chem., 1935, **39**, 289—292).—Expressions for the coeff. of diffusion of charged and uncharged particles in a motionless medium have been deduced. Preliminary results of colorimetric measurements of the penetration of $CuCl_2$ into gels indicate the utility of the equation. M. S. B.

Colloidal properties of the pectins. J. Bonner (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 346—354).—The prep. of Na pectate (I), pectic acid (II), a pectinic acid (III), and a Na pectinate (IV) is described. A slight discrepancy between the reciprocal hexol no. (V) of (II) and its equiv. wt. may be due to adsorption of OH′ as this discrepancy decreases with increasing acidity. $Th^{\cdot\cdot\cdot\cdot}$ also reverses the charge of (II). Luteo-$Co^{\cdot\cdot\cdot}$ and $Ca^{\cdot\cdot}$ reduce but do not reverse the charge. The equiv. wt. of (I) obtained by direct titration is > that obtained by back titration with NaOH, and depends on the period of drying owing to anhydride formation. The vals. of (V) for (III) and (IV) are much larger and, in agreement with their smaller charge density, their sols are not so readily pptd. by electrolytes. (III) forms complex and auto-complex coacervates. E. A. H. R.

Combining weight of collagen.—See this vol., 769.

Theory of Liesegang rings. E. B. Hughes (Kolloid-Z., 1935, **71**, 100—103).—Analyses carried out at different depths of penetration into the gel are in accordance with the diffusion law. Basing the theory on this law, the distances between the bands are accounted for. E. S. H.

Calculation of the gaseous equilibrium $\frac{1}{2}I_2+\frac{1}{2}Br_2=IBr$. H. Zeise (Z. Elektrochem., 1935, **41**, 267—270).—From the calc. val. of the moment of inertia of IBr, 493×10^{-40} g.-cm.^{2}, and the heat of formation, 1380 g.-cal., deduced from microscopic data, vals. of K_p for temp. 298—2000° abs. have been obtained in good agreement with experimental results. M. S. B.

Heat capacities and dissociation equilibria of gases. B. Lewis and G. von Elbe (J. Amer. Chem. Soc., 1935, **57**, 612—614).—Data representing the energy content are given for H_2, O_2, N_2, CO, NO, OH, CO_2, H_2O, O_3, Br, and HBr from 200° to 3500° abs. and the consts. for equilibria involving these gases and also Cl_2 and HCl from 300° to 5000° abs. E. S. H.

Extremely small concentrations and the law of mass action. Ionic theory. I. M. Kolthoff (Chem. Weekblad, 1935, **32**, 246—249).—The actual physical significance of concns. of the order of 10^{-25} is discussed and the evidence for their real existence and for the general validity of the law of mass action as applied to electrolytes is reviewed. D. R. D.

Acids, bases, and salts. M. Kilpatrick (J. Chem. Educ., 1935, **12**, 109—111).—A discussion. L. S. T.

Activity and osmotic coefficients of strong and weak electrolytes. P. van Rysselberghe (J. Physical Chem., 1935, **39**, 403—414).—Thermodynamic relations between the activity coeffs. and the osmotic coeffs. for undissociated, completely dissociated, and incompletely dissociated solutes have been derived using Gibbs' method. Simple formulæ have been deduced which are applicable at very low concn. or to a very weak electrolyte. Comparison is made with Lewis and Randall's method. M. S. B.

Dissociation of carbamide in dilute solution. P. Cristol, J. Fourcade, and R. Seigneurin (Compt. rend., 1935, **200**, 1369—1370).—The lowering of f.p., conductivity, and p_H vals. of solutions of carbamide in H_2O and in 0·9% aq. NaCl indicate an equilibrium represented by $NH{:}C\langle^{NH_3}_{O}\rightleftharpoons NH{:}C(NH_2)\cdot OH\rightleftharpoons NH{:}C(NH_2)\cdot O^-+H^+$. F. R. G.

Transmission of polar effects through space. I. Jones and F. G. Soper (Chem. and Ind., 1935, 342—343).—The polar effect on the primary ionisation const. for a no. of org. acids varies inversely as the cube of the distance between the polar groups, independently of the no. of intervening C atoms. C. W. G.

Slow hydrolysis: constitution and progressive change of aqueous solutions of stannic chloride. J. Guéron (Ann. Chim., 1935, [xi], **3**, 225—326).—Freshly formed aq. solutions of $SnCl_4$, and the changes they undergo with time, have been studied by centrifuging, ultrafiltration, measurements of p_H, coagulation by Na_2SO_4 and by a glass surface, photometric measurements, viscosity determinations, and by examination of Raman spectra. Fresh solutions of $SnCl_4$ contain very few mols. of the salt but large quantities

of the ions $SnCl_6''$ (I). These gradually disappear by hydrolysis and, after a period of induction, coagulation of the products of hydrolysis takes place. The process is autocatalytic and the walls of the vessel have a catalytic effect. The initial period of stabilisation of the solutions is due to the appearance in the solution of $Sn^{\cdots\cdot}$, probably as a result of the decomp. of the complex (I). When these ions in turn are removed by hydrolysis, coagulation takes place. In the stage preceding pptn. the solutions become thixotropic. "Slow hydrolysis," considered as a reaction which is sp. for solutions in which the product of hydrolysis is colloidal, does not exist. Previous study of the phenomenon in the more complicated case of $FeCl_3$ exclusively, has prevented the recognition of the two separate stages. M. S. B.

Sodium aluminate. A. Maffei (Gazzetta, 1935, **65**, 108—116; cf. A., 1934, 732).—The hydrolysis of Na aluminate in solutions obtained by dissolving Al in NaOH has been studied potentiometrically, and is shown to be more complicated than in ordinary solutions containing excess of NaOH. O. J. W.

Concentration of hydrogen ions in aqueous solutions of complex cobaltammines and their absorption spectra. II. T. Uémura and H. Suéda (Bull. Chem. Soc. Japan, 1935, **10**, 85—97).—The relation between the coeff. of extinction and λ, for solutions of the following complex salts, has been studied by the method previously described (this vol. 579): $[Co(NH_3)_3(H_2O)_3]Cl_3$ (*cis* and *trans*) (I), $[Co_2(NH_3)_6(OH)_3]Cl_3$ (II), $[Co\{Co(NH_3)_4(OH)_2\}_3]Cl_6$ (III), $[Co(NH_3)_3(H_2O)Cl_2]Cl$ (blue, grey, and black) (IV), $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$ (V), $[Co(NH_3)_3(H_2O)_2Cl]SO_4$ (violet and blue-grey) (VI), $[Co(NH_3)_3(H_2O)Cl_2]SO_4H$ (VII). Practically no change takes place in these solutions and those previously studied (*loc. cit.*) at $p_H<7$. Above p_H 7 the triammines, except *trans*-(I), seem to change into polynuclear complexes in which the central atoms are linked by OH. (IV) and (V) give similar extinction curves in solution, as also do (VI) and (VII). The curves for (II) and (III) show characteristics previously noted for polynuclear complexes. Their absorption is stronger than for ordinary complexes and there is practically no absorption in the ultra-violet. M. S. B.

Hydrolysis of inorganic salts and the chemistry of the high-molecular hydrolysis products (including *iso*- and heteropoly-compounds). II. G. Jander and K. F. Jahr (Kolloid-Beih., 1935, **41**, 297—354; cf. this vol., 181).—A review of published works, particularly on the complex acids of Mo, W, and V. The co-ordination formulæ of the complexes are discussed. E. S. H.

Equilibria of basic amino-acids in the formol titration. M. Levy (J. Biol. Chem., 1935, **109**, 365—381; cf. A., 1933, 381; Birch *et al.*, A., 1930, 1458).—The procedure and theoretical considerations previously applied to other NH_2-acids are extended to arginine, lysine, and histidine. W. McC.

Titration constants of glyoxaline derivatives. M. Levy (J. Biol. Chem., 1935, **109**, 361—363).—The consts. for 4-(or 5-)methylglyoxaline, iminazolyl-lactic acid, histamine, and histidine have been determined by electrometric titration. W. McC.

Ampholytic nature of phospholipins. H. Fischgold and E. Chain (Proc. Roy. Soc., 1935, **B**, **117**, 239—257).—By titration in C_6H_6–EtOH solution both the acid- and base-binding properties of phospholipins (I) may be determined. The (I) examined react with 1 equiv. of H^+, but only those with a primary NH_2 react with alkali. It is inferred that the (I) containing a quaternary NH_4 base can exist only as cations or zwitterions, whilst those containing primary NH_2 can exist as zwitterions, neutral mols., anions, or cations. F. A. A.

Binary system strontium nitrate–strontium hydroxide. G. Wolf (Compt. rend., 1935, **200**, 1203—1205).—The fusion diagram of the system shows a max. at 30·5% $Sr(NO_3)_2$, corresponding with $Sr(NO_3)_2,4Sr(OH)_2$. J. W. S.

Binary system lead iodide–lead oxide. H. S. van Klooster and R. M. Owens (J. Amer. Chem. Soc., 1935, **57**, 670—671).—PbI_2,PbO decomposes at 465° yielding PbI_2,2PbO (m.p. 620°). The existence of PbI_2,4PbO (m.p. 650°) is tentatively indicated. A eutectic occurs at 30 mol.-% PbO and 365°. E. S. H.

Fusion diagram of the system ZrO_2–SiO_2. N. Shirnova (J. Gen. Chem. Russ., 1934, **4**, 1464—1470).—The compound $ZrSiO_4$, m.p. 2430°, is confirmed, and eutectics at 2220° and 1705° with 42 and 97 mol.-% SiO_2 are recorded. R. T.

Thermal decomposition of palladium chloride and chloro-salts. F. Puche (Compt. rend., 1935, **200**, 1206—1208).—The dissociation of $PdCl_2$ begins at 600° and the dissociation pressure reaches atm. at 920°. The log p–$1/T$ curves show that the m.p. of $PdCl_2$ is 936°, the latent heat of fusion 9, and the heat of formation of solid $PdCl_2$ 26·3 kg.-cal. per mol. The heats of formation of K_2PdCl_4 and K_2PdCl_6 are 52·67 and 79·06 kg.-cal. per mol., respectively. K_2PdCl_6 dissociates into K_2PdCl_4 above 175°. J. W. S.

Phase diagrams of certain organic binary systems. XXII. N. A. Pushin and L. Sladović (Bull. Soc. Chim. Yougoslav., 1934, **5**, 135—141).—The m.-p. diagrams do not indicate compound formation in the systems *p*-cresol–resorcinol, –phenanthrene (I), *o*-cresol–(I), borneol–$C_{10}H_8$, –$NHPh_2$, –urethane, BzOH–α- and β-$C_{10}H_7$·NH_2. R. T.

Thermal analysis of the system antipyrine–trichlorobutyl alcohol. A. Rychterówna (Wiad. farm., 1934, **61**, 95—97; Chem. Zentr., 1934, ii, 3647—3648).—No mol. compounds are formed. Eutectic mixtures containing (i) 40 mol.-% antipyrine (I) and (ii) 2 parts of (I) and 3 parts of trichlorobutyl alcohol have been observed. A. G. P.

Equilibrium of sodium sulphate, sulphuric acid, and water, and the causticising of sodium sulphate. T. Okuno (Mem. Fac. Eng. Kyushu, 1935, **7**, 275—355).—The ternary system has been studied at 25°, and for the lower concns. at 5—25°. The decomp.–time curves of $NaHSO_4$ have been determined at 300—600°, $Na_2S_2O_7$ being formed at 300° and Na_2SO_4 at higher temp. *X*-Ray studies show that all

solid phases are converted into Na_2SO_4 after heating at 420—500°. The recovery of coagulation solutions (containing Na_2SO_4) used in the artificial silk industry is discussed. The dissociation pressure of the system $2NaHSO_4(s) \rightleftharpoons Na_2S_2O_7(s)+H_2O(g)$ at 135—196° is given by $\log p_{mm.} = -4303{\cdot}9/T+10{\cdot}7436$ in agreement with vals. calc. by the Nernst theorem. For $Na_2S_2O_7(s) \rightleftharpoons Na_2SO_4(s)+SO_3(g)$ at 330—380° $\log p_{mm.} = -7132{\cdot}44/T+12{\cdot}125$, and for $NaHSO_4(s)+NaCl(s) \rightleftharpoons Na_2SO_4(s)+HCl(g)$ at 130—255° $\log p_{mm.} = -5391{\cdot}84/T+13{\cdot}5313$. The reduction of Na_2SO_4 by CO and by C has been studied at 700—900°, the reactions $Na_2SO_4+4CO \longrightarrow Na_2S+4CO_2$ and $Na_2SO_4+4C \longrightarrow Na_2S+4CO$ being accompanied by $3Na_2SO_4+Na_2S \longrightarrow 4Na_2O+4SO_2$, $4Na_2O+4CO_2 \longrightarrow 4Na_2CO_3$, $4SO_2+8CO \longrightarrow 8CO_2+2S_2$, $2CO \rightleftharpoons CO_2+C$. A max. yield of Na_2S is obtained with $3Na_2SO_4$: 1C at 850° for 40 min., the yield decreasing with time. Reduction of Na_2SO_3 by CO and C has also been studied. The const., $[S'']/[OH']^2$, for the reaction $Na_2S+CuO+H_2O \longrightarrow 2NaOH+CuS$ in solution is approx. $8{\cdot}5\times10^{-31}$. The influence of concn. is small, and the yield decreases slightly with rising temp. The oxidation of CuS by O_2 gives CuO at 800°, but at lower temp. $CuSO_4$ is formed; at > 1100° CuO decomposes into Cu_2O and O_2. For the reduction of $BaSO_4$ by CO, $\log(p_{CO_2}/p_{CO}) = 1111/T+5{\cdot}125-1{\cdot}76\times\log T+6{\cdot}65\times10^{-4}T-7{\cdot}75\times10^{-8}T^2$, calc. by theory and in fair agreement with the author's experiments. In addition to the main reaction $BaSO_4+4CO \longrightarrow BaS+4CO_2$ side reactions occur. The yield is a max. at 850° and decreases with time. A good yield of BaS is possible with only 15% of CO. The reaction $BaS+CuO+H_2O \longrightarrow 2NaOH+CuS$ has been studied, with results similar to those with $Na_2S+CuO+H_2O$. The const., $[OH']^2/[SO_4'']$, for the reaction $Ba(OH)_2+Na_2SO_4 \longrightarrow BaSO_4+2NaOH$ in solution is approx. $1{\cdot}2\times10^8$. A good yield of NaOH is obtained.

R. S. B.

Ternary systems. XX. Calcium sulphate, ammonium sulphate, and water. A. E. Hill and N. S. Yanick (J. Amer. Chem. Soc., 1935, **57**, 645—651).—Equilibrium data for 100°, 75°, 50°, and 25° are recorded. No new solid phases are reported.

E. S. H.

Liquid–solid equilibria in the system naphthalene–α-naphthol–β-naphthol. K. Hrynakowski and M. Szmyt (Z. physikal. Chem., 1935, **173**, 58—66).—Data for the ternary equilibrium are recorded.

R. C.

Thermal equilibria in ternary systems. III. Phenacetin–antipyrine–urethane. K. Hrynakowski and F. Adamanis [with A. Denizot and B. Marcinkowski (Rocz. Chem., 1935, **15**, 44—51).—Compound formation is not observed; the ternary eutectic mixture, m.p. 29°, contains phenacetin 8·5, antipyrine 36, and urethane 55·5%. R. T.

Oxidation–reduction equilibrium of metallic chromium. S. Aoyama and E. Kanda (J. Chem. Soc. Japan, 1934, **55**, 1174—1184).—The equilibrium $2Cr+3H_2O \rightleftharpoons Cr_2O_3+3H_2$ has been studied at low temp.; the data lead to $\Delta F_{298} = -112{,}502$ g.-cal. and $\Delta H_{298} = -107{,}980$ g.-cal. Vals. for the v.p. of ice (166·5—264·5° abs.) are recorded. Ch. Abs. (*e*)

Constitution of glasses. E. Jenckel (Z. Elektrochem., 1935, **41**, 211—215; cf. A., 1934, 965).—Property–composition curves for a series of glasses, viz., B_2O_3–Na_2O,$2B_2O_3$, B_2O_3–BaO,$2B_2O_3$, B_2O_3–PbO, B_2O_3–SiO_2, SiO_2–Na_2O,B_2O_3, B_2O_3–Na_2O,SiO_2, and Na_2O,SiO_2–SiO_2, indicate the existence of definite compounds. The properties studied were the transformation temp., sp. vol., coeff. of expansion, and reciprocal refractive index. F. L. U.

Oxidising power of basic slags. I. Determination of the binary diagram CaO–Fe_2O_3. II. Determination of the dissociation pressures of Fe_2O_3, CaO,Fe_2O_3, and $2CaO,Fe_2O_3$. J. White, R. Graham, and R. Hay (Iron and Steel Inst., May 1935, Advance copy, 21 pp.).—I. On prolonged heating of 1 : 1 mol. mixtures of CaO and Fe_2O_3 at 1000° a dark powder is formed which melts at 1250° and solidifies to hard black needles of CaO,Fe_2O_3. Optical evidence of $2CaO,Fe_2O_3$, formed by a peritectic reaction at 1450°, has also been obtained. A eutectic occurs at 90% Fe_2O_3, 1210°; Fe_2O_3 melts at 1595° with decomp.

II. Fe_2O_3 dissociates appreciably at 1100° and at the m.p. the dissociation pressure is about 5×10^5 atm. Fe_2O_3 and Fe_3O_4 appear to be mutually sol.; the solubilities increase rapidly between 1050° and the liquidus line at about 1520°. The pressure of O_2 from the two Ca ferrites is negligible below the peritectic temp.; at higher temp. the amount of Fe_2O_3 liberated by the peritectic reaction determines the dissociation pressure. A. R. P.

Heat and free energy of formation of arsenic trifluoride. D. M. Yost and J. E. Sherborne (J. Amer. Chem. Soc., 1935, **57**, 700—701).—For gaseous AsF_3, $\Delta H = -191{,}300$ g.-cal.; $\Delta F_{298} = -188{,}000$ g.-cal. E. S. H.

Heat evolved in metallic transformations. II. Cobalt. H. von Steinwehr and A. Schulze (Physikal. Z., 1935, **36**, 307—311; cf. A., 1934, 725; B., 1934, 764).—The heat evolved in the transition of α- into β-Co is $0{\cdot}1\pm0{\cdot}03$ g.-cal. per g., and in the transition from the ferromagnetic to the paramagnetic state, $1{\cdot}2\pm0{\cdot}07$ g.-cal. per g. The α–β transition takes place at 380—420°, and the magnetic transition at 1070—1125°. A. J. M.

Latent heat of fusion of equilibrium mixtures of light and heavy water. L. Jacobs (Trans. Faraday Soc., 1935, **31**, 813—821).—Mol. heats of fusion (*L*) of mixtures containing up to 97·7 mol.-% of D_2O have been determined. The extrapolated val. of *L* for 100% D_2O is 1525 ± 2 g.-cal. F. L. U.

Specific heat of a liquid and its vapour and its application to the heat of reaction in liquid mixtures. D. B. Macleod (Trans. Faraday Soc., 1935, **31**, 746—748).—There is a nearly const. difference of about 9 g.-cal. between the mol. heats of different liquids and their respective vapours at the ordinary temp. This difference, which cannot be accounted for by expansion against internal forces in the liquid, is due to extra degrees of freedom in the liquid state. The origin of these is discussed, and it is shown that they account for the approx. equality of

heats of reaction between the components of widely different liquid mixtures. F. L. U.

(A) Determination of the heat capacity of aqueous solutions and the heat of dissolution of salts. M. M. Popov, K. G. Khomjakov, N. N. Feodosiev, and P. K. Shirokikh. **(B) Heat capacity of aqueous solutions of phosphoric acid.** M. M. Popov, N. N. Feodosiev, and S. M. Skuratov (Trans. Sci. Inst. Fertilisers U.S.S.R., 1933, No. 110, 12—23, 23—34).—(A) A comparison of experimental methods.

(B) Data are recorded for aq. H_3PO_4 (0—89·72%). Ch. Abs. (e)

Heats of dissolution and of dilution of potassium and ammonium phosphates. K. G. Khomjakov, S. F. Javorovskaja, and P. K. Shirokikh (Trans. Sci. Inst. Fertilisers U.S.S.R., 1933, No. 110, 34—46).—In addition to the thermal data, the solubilities of K_3PO_4, K_2HPO_4, and $NH_4H_2PO_4$ are recorded. Ch. Abs. (e)

Temperature variation in transference numbers of concentrated solutions of sulphuric acid as determined by the galvanic cell method. W. J. Hamer (J. Amer. Chem. Soc., 1935, **57**, 662—667).—Transference nos. have been calc. from e.m.f. data for the cell $Hg|Hg_2SO_4|H_2SO_4(m)|H_2SO_4(m')|Hg_2SO_4|Hg$ over the range 0·05—17·0M and at 0°, 10°, 15°, 25°, 35°, 45°, and 60°. Extrapolations of the $H^{\cdot}$ transference nos. to zero concn. and the limiting law based on the Debye–Hückel–Onsager conductance equations are given at various temp. E. S. H.

Mechanism of conductance. H. S. Lukens (Trans. Electrochem. Soc., 1935, **67**, 317—324).—By plotting the equipotential lines between two electrodes placed in an electrolyte, it has been shown that their contour is the same as in solid conductors in similar circumstances. The mechanism of electrolytic conductance is discussed in the light of this result. E. S. H.

Properties of electrolytic solutions. XVI. Conductance of electrolytes in anisole, ethylene bromide, and ethylene chloride at 25°. N. L. Cox, C. A. Kraus, and R. M. Fuoss (Trans. Faraday Soc., 1935, **31**, 749—761; cf. this vol., 302).—Conductivities of several tetra-alkylammonium salts have been measured at concns. ranging from $1·6\times10^{-2}$ to $1·3\times10^{-6}N$. The results are in accord with the ion association theory developed by Fuoss and Kraus. Ion dimensions calc. from the consts. of the association equilibria agree with accepted at. dimensions. F. L. U.

Conductivity of methoxides and ethoxides. W. F. K. Wynne-Jones (J.C.S., 1935, 540).—The results of Jones *et al.* (A., 1934, 1071) are in good agreement with those of the author (A., 1928, 22), but their statement as to the author's correction for solvent conductivity is not correct. There appears to be no experimental basis for their assumption as to the amount of NH_3 probably present as impurity in MeOH. M. S. B.

Surface conductivity at solid–liquid interfaces. F. Urban, H. L. White, and E. A. Strassner (J. Physical Chem., 1935, **39**, 311—330).—The sp. surface conductivity (I) of Pyrex glass particles in aq. KCl and NaCl, concn. $1·25\times10^{-4}$—$1\times10^{-2}M$, has been determined using 1000-cycle a.c. (I) represents the same fraction of total conductivity as in a glass capillary of about 10 μ diameter. An equation for calculating (I) on the basis of the Stirn double layer has been developed and the calc. vals. are in good agreement with experiment, but the vals. calc. according to Gouy's theory are not. The sedimentation vol. decreases with increase of concn., but in KCl there is a sharp rise in vol. between 3×10^{-3} and $1\times10^{-2}M$. It is shown that this is probably not due to a "Hafteffekt." The thickness of the double layer for various concns. of KCl has been calc. M. S. B.

Magnitude of surface conductivity. J. W. McBain and J. E. Foster (J. Physical Chem., 1935, **39**, 331—342).—A.c. measurements of the sp. surface conductivity (I) at 25°, of KCl of different concn., at a glass–solution interface, give vals. varying from $9·96\times10^{-8}$ to 264×10^{-8} for concn. 0·001—0·1N, in confirmation of previous results (A., 1930, 37, 704). The high results are in part due to irregularities at the surface of the glass as compared with the optically polished glass previously used. (I) at an air–H_2O interface (an ideally plane surface) is $3·8\times10^{-8}$ for a closely packed film of stearic acid, $4·0\times10^{-8}$ for palmitic, and $8·4\times10^{-8}$ for oleic. The vals. are far > those calc. on the basis of current theories of the mobility of the ions in the outer portions only of the diffuse double layer. New cell designs are described. M. S. B.

Nature of the residual current observed with Zlotowski's moving cathode. N. Thon (J. Chim. phys., 1935, **32**, 269—272).—Contrary to Zlotowski (this vol., 171) it is suggested that the residual current is partly non-faradic, and the formula of Z has been derived on this basis. R. S.

Transport of electricity through phase boundaries. System I: glass–gas or vapour. II. Electrolytic introduction of hydrogen, nitrogen, and potassium into a glass diaphragm, and electrolytic transport of sodium through a glass diaphragm. C. Stüber (Z. physikal. Chem., 1935, **172**, 401—428; cf. A., 1932, 230).—Experiments have been made on the passage of a glow d.c. discharge through a gas between a metal anode and a glass diaphragm backed by a metal cathode, the positive electricity carriers produced in the discharge being thereby introduced into the glass and replacing the alkali ions. Faraday's law is valid for the discharge of $Na^{\cdot}$ and $K^{\cdot}$ at the cathode and for the migration of $Na^{\cdot}$, $K^{\cdot}$, and $H^{\cdot}$ from the gas phase into the glass. N migrates into the glass, but He, O, CO_2, and CCl_4 do not. When cations do not migrate into the glass in electrolysis, $SiO_3(SiO_2)_x$ radicals are formed at the anode side of the glass and at higher temp. give $SiO_2(SiO_2)_x+O$. The disappearance of gases in the electrolysis cannot be explained by occlusion, diffusion, or clean-up effects. By electrolysis of Na and K vapours photo-electric cells having characteristics similar to those recorded in the literature have been prepared. R. C.

Hydrogen electrodes. M. Volmer and H. Wick (Z. physikal. Chem., 1935, **172**, 429—447).—For

bright Pt, Ir, and Au electrodes in specially purified aq. H_2SO_4 the c.d.–potential curves (I) for the discharge and dissolution of H are linear in the immediate vicinity of the equilibrium potential, as Volmer's theory of overvoltage requires (cf. A., 1933, 1122). At higher c.d. the discharge curves assume a pure logarithmic form, but the dissolution curves diverge from this form, due probably to retardation of $H_2 \longrightarrow 2H$. Investigation of poisoning by As_2O_3 has shown that the effect of poisons on the kinetics of H discharge and dissolution consists in a raising of the energy threshold together with displacement of the latter in the double layer. Retardation of $2H \longrightarrow H_2$ is probable, but has not been proved. Under the conditions under which H overvoltage at solid electrodes is measured, the electrode surface is almost always partly covered with impurities from the electrolyte. R. C.

Adsorption electrodes. II. Mineral electrodes. H. J. C. Tendeloo (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 434—441; cf. A., 1934, 749).—A thin plate of mica immersed in 0·1*N*-H_2SO_4 for 2 days behaves as a H electrode, with $\log E \propto \{[H_2SO_4]+\text{const.}\}$. Similarly, after immersion in slightly alkaline $CaCl_2$ the mica functions as a Ca electrode. Heavy spar, CaF_2, and wollastonite were also studied as electrodes. R. S. B.

Periodic changes of potential of iron in nitric acid. I. M. Karschulin (Z. Elektrochem., 1935, **41**, 224—229; cf. A., 1934, 1072).—Oscillations of potential occurring when Fe is immersed in aq. HNO_3 (36—56 wt.-%) are influenced by concn., temp., and by whether the Fe is partly or completely immersed. The Fe becomes covered with a brownish layer during periods of increasing positive potential, which reaches a max. when the layer is destroyed by a sudden evolution of gas. The cycle is then repeated. During the dissolution of Fe in 41·7% HNO_3 evolution of gas occurs alternately on sharply bounded adjacent areas of metal. The results are discussed. F. L. U.

Mechanism of appearance of potential [at metallic electrodes] in solutions containing foreign ions. O. Essin and T. Beklemischeva (J. Gen. Chem. Russ., 1934, **4**, 1394—1399).—The e.m.f. of Ag electrodes in aq. $CuSO_4$ and $Cu(NO_3)_2$ is given by $E_{Ag|CuX}=a+bE_{Cu|CuX}$, where X is one of the above anions; the results are in accordance with those recorded for Au electrodes (this vol., 449), and by Schmid for Cu electrodes in aq. K and Na halides (A., 1933, 28, 354, 677). R. T.

Sodium discharge potential at the mercury cathode. W. W. Stender, M. M. Stroganov, and P. B. Zivotinsky (Trans. Electrochem. Soc., 1935, **68**, 23—33).—In 4·28*N*-NaCl solutions at 15°, 50°, and 70° with c.d. 2·88—30 amp. per sq. dm. the Na discharge potential at an amalgam cathode (0·02—0·4% Na) ranges from 0·1 to 0·15 volt. Overvoltage is essential to amalgamation and explains the progressive departure of the cathode potential from the equilibrium val. with increase in c.d. J. W. C.

Relations between fundamental electrochemical quantities. I. Uhara (J. Chem. Soc. Japan, 1934, **55**, 1207—1222).—Theoretical. An expression is obtained which relates the electrode potential of a metal with the heat of formation of a salt of the metal, and its solubility in the solvent. Examples are discussed. Ch. Abs. (*e*)

Electrode potential of ascorbic acid. N. Bezssonoff (J. Chim. phys., 1935, **32**, 210—214).—The oxidation-reduction potential curve of ascorbic acid against log. concn. consists of two inclined straight lines. Results of previous workers fall on one or other of these. The effect is ascribed to the presence of two reducing groups in the mol. D. R. D.

Oxidation of solutions of quinol. II. Physicochemical study of alkaline solutions of quinol. A. Saint-Maxen (J. Chim. phys., 1935, **32**, 273—284; cf. A., 1934, 8).—Conductivity and spectrophotometric data are given for aq. mixtures of quinol and bases. Acid (I) and neutral salts of quinol are formed, (I) having max. oxidisability. An oxidation mechanism involving a quinonoid form is suggested. R. S.

Electrolytic reduction potentials of organic compounds. XX. Reduction potential of quinine. M. Shikata and E. Taguchi (J. Electrochem. Assoc. Japan, 1934, **2**, 234—239; cf. this vol., 305).—Reduction of quinine (I) occurs in 3 stages, in the first of which 2 H are required to reduce 1 mol. of (I) at p_H 8·1—10·8; the reduction potentials obey the Nernst formula. Ch. Abs. (*e*)

Oxidation and reduction with hydrogen peroxide. W. D. Bancroft and N. F. Murphy (J. Physical Chem., 1935, **39**, 377—397).—It is shown that, when the true e.m.f. of any oxidising or reducing agent in any solution is > the true e.m.f. of H_2O_2 in the same solution, that substance will be reduced by H_2O_2; if the converse is the case then it will be oxidised. The true e.m.f., relatively to the H electrode, of H_2O_2 in *M*-HCl or -H_2SO_4 is $+1·16\pm0·03$ volt and in *M*-KOH $+0·30\pm0·02$ volt, not correcting for the diffusion potential. The primary reaction in the O_2–H_2 gas cell is the formation of H_2O_2. H_2O_2 is considered as dissociating reversibly into $2H+O·O$. The singly linked O_2 is in an activated state. 2H is the reducing and O·O the oxidising agent. Numerous chemical reactions in which H_2O_2 takes part are discussed. M. S. B.

Polarographic studies with the dropping mercury cathode. XLVI. Current–voltage curves using small anodes. V. Majer (Coll. Czech. Chem. Comm., 1935, **7**, 146—157).—As the size of the anode is diminished to that of the dropping cathode, the diffusion currents, *i*, are not altered, but the current increments corresponding with the deposition of various metals are displaced towards larger e.m.f. vals. as the result of increase of resistance, or concn. polarisation. Hg droplets falling on the anode change the potential owing to stirring and the negative charge carried by the droplets. With very small vols. of solution, *i* decreases with time. J. G. A. G.

Influence of depolarisers on the photovoltaic effect in cells containing Grignard reagent. J. Harty (J. Physical Chem., 1935, **39**, 355—

369).—Electrodes of Cu, Zn, Al, Fe, Pb, and Pt have been used in combination with MgEtBr and MgPhBr as electrolytes and EtBr and EtI as depolarisers. Voltage, current, resistance, and capacitance response to light under different conditions have been studied. The results are in accordance with Hammond's assumption (A., 1930, 846) of the presence of a unimol. layer of electrolyte on the surface of the electrode. If light produces, in or near this layer, excited mols. with dipole moments different from those of normal mols., and capable of displacing the latter, a change in the potential of the electrode will result. If the life period is short the electrode will recover in the dark and return to normal potential. Change in a.c. resistance must be due to change in the electrolyte, which probably consists in a change in the solvation and hence in the mobility of the ion. The formation or alteration of a double layer in the light would explain negative capacitance response, and difference in orientation of the mols. would explain the existence of positive and negative voltage and current responses. M. S. B.

Hydrogen overvoltage. P. P. Porfirov (Compt. rend. Acad. Sci., U.R.S.S., 1935, **1**, 386—392).—Observations on the electrolysis of H_2SO_4 between a platinised Pt anode and Hg cathode show the existence of a contact resistance; this, however, is only contributory to the H overvoltage and is due to a film of H_2 which begins to form at low cathode polarisation. It decreases with increase in the c.d. and its max. coincides with the beginning of the increase in the current strength on the potential–c.d. curve. W. R. A.

Delayed ionic discharge as cause of hydrogen overvoltage and of cathodic polarisation generally. A. Smits (Z. physikal. Chem., 1935, **172**, 470—472).—A claim for priority over Erdey-Grúz and Volmer (A., 1930, 1376). Smits' theory of electromotive equilibria also explains the primary process of anodic polarisation. R. C.

Overvoltage. VIII. Overvoltage at bright platinum electrodes in 2*N*-H_2SO_4 for low c.d. determined with an oscillograph. A. L. Ferguson and G. M. Chen (J. Physical Chem., 1935, **39**, 191—198).—Charge and discharge curves showing the influence of time and c.d. are given. A comparison is made of the direct, commutator, and electromagnetic interrupter methods of studying overvoltage. A distinction between discharge curves due to pure resistance, those due to true depolarisation, and those due to a combination of the two is attempted. It is concluded that there is no transfer resistance at the surface of smooth Pt electrodes. M. S. B.

Rôle of transitory resistance in the phenomenon of overvoltage of hydrogen. P. P. Porfirov (J. Gen. Chem. Russ., 1934, **4**, 1311—1321).—The transitory resistance (I) established at a Hg cathode as a result of the formation of a film (II) of H_2 is not the sole cause of H overvoltage. The commencement of (II) formation is associated with insignificant cathodic polarisation. For d.c. the val. of (I) diminishes with increase in the c.d. R. T.

Overvoltage of halogens. F. T. Chang and H. Wick (Z. physikal. Chem., 1935, **172**, 448—458).—Overvoltage has been observed for Cl on bright Pt, and Cl and Br on Ir. The anodic overvoltage curves have a logarithmic character, which for Pt, however, is obliterated at higher c.d. by passivity phenomena. The cathodic curves deviate from the logarithmic form in the same way as those for H overvoltage (cf. this vol., 705) and can be represented approx. by $\eta=a-b\log I-cI$, where η is the potential and I the current and a, b, and c are consts. Possibly the term cI is due to supplementary retardation of $X_2\longrightarrow 2X$. The results obtained cannot be covered either by Tafel's or Volmer's theory of overvoltage. R. C.

Effect of an electric current on a protein cylinder according to Bois-Reymond. W. Habenicht (Protoplasma, 1934, **22**, 321—336).—A study has been made of the changes involved in the anodic shrinkage and cathodic expansion of small cylinders of ovalbumin carrying an electric current. The migration of H_2O and the effect of products of hydrolysis are considered. A. G. P.

Electromotive force produced by the flow of water vapour. A. Milhoud (Compt. rend., 1935, **200**, 1091—1093).—The production of electrical effects by the turbulent escape of H_2O vapour, through a blow-pipe of constricted section, has been confirmed (cf. *ibid.*, 1934, **198**, 1586). In the presence of droplets an e.m.f. is set up which depends on the electrical conductivity of the solution. The concn. of the solution must be $\not>$ 0·001*N*. For any one solution $E/(P_c-p)$ is a const. where E=e.m.f., P_c=crit. pressure, and p=escaping pressure. The acidity of the solution affects the polarity. H_2O alone and acid solutions give a positive and basic solutions a negative jet. With such solutions 0·01 volt may be obtained. M. S. B.

Absolute rate of a chemical reaction. W. H. Rodebush (J. Chem. Physics, 1935, **3**, 242).—The different methods of approach to the study of the factors determining the abs. rate of a chemical reaction are indicated. M. S. B.

Reaction mechanisms. C. C. Steffens (J. Chem. Educ., 1935, **12**, 115—120).—A review of recent ideas on reaction rates and mechanisms, particularly with regard to homogeneous gas reactions. L. S. T.

Application of Bodenstein's method of stationary concentrations of intermediate products in reaction kinetics. J. A. Christiansen (Z. physikal. Chem., 1935, **B**, **28**, 303—310).—The concept of "reaction sequences" is discussed and illustrated. R. C.

Measurement of reaction kinetics by means of light absorption. S. Bodforss (Svensk Kem. Tidskr., 1935, **47**, 33—41).—A crit. survey of the methods available, especially those involving photoelectric cells. R. P. B.

Reaction cycles. A. Skrabal (Monatsh., 1935, **65**, 275—310).—Theoretical. A mathematical study of reactions the simplest of which is exemplified by the interconversion of three tautomerides. E. S. H.

Mechanism of self-propagating chain reactions. K. K. Andreev and J. B. Chariton (Trans. Faraday Soc., 1935, **31**, 797—804; cf. A., 1934, 602).—Theoretical. An attempt is made to estimate the size of the localisation of chain centres required to initiate the detonation of an explosive by a macro-chain mechanism. F. L. U.

Kinetics of heterogeneous ortho-para-hydrogen transformation on solid oxygen. E. Cremer (Z. physikal. Chem., 1935, **B**, **28**, 383—392; cf. this vol., 586).—The rate of transformation at H_2 pressures of 50—760 mm. over solid O_2 at 20° abs. as catalyst has been measured. The results indicate that reaction occurs in an adsorbed film saturated with o-H_2. There is very little adsorption of p-H_2 or adsorption displacement of o- by p-H_2. The heat of adsorption of o-H_2 is 428 ± 10 and that of p-$H_2 < 326$ g.-cal. The velocity is 10^4—10^5 as great as would be deduced from the frequency of collisions with the catalyst surface, the reason being that in the adsorbed state as compared with the gaseous state the ratio of the duration of collision between H and O mols., τ, to the time between two collisions is shifted in favour of τ, because in the adsorbed film the H is always in the sphere of action of the O. R. C.

Effect of frequency of the electric field on the velocity of combustion of gases. A. E. Malinovski, V. S. Rossikhin, and V. P. Timkovski (Physikal. Z. Sovietunion, 1934, **5**, 902—905).—The burning of a 25% C_2H_2–75% air mixture was studied in fields of frequency 10^5—$0{\cdot}8\times10^7$ Hertz units. The velocity was lowered 6·7% at 10^5 and 0·6% at 10^7 Hertz units. Ch. Abs. (*e*)

Lower limit of ignition of hydrogen–oxygen mixtures. W. E. Garner and H. J. Willavoys (Trans. Faraday Soc., 1935, **31**, 805—811; cf. A., 1931, 688).—The lower limits for ignition of H_2–O_2 mixtures in mol. ratios 3 : 1, 2 : 1, 1 : 1, and 1 : 2 in the temp. range 350—600° are lower than those found by previous workers. The activation energy decreases with rise of temp. from 15 to 7 kg.-cal. Vals. of the limits near the crit. ignition pressure are greatly influenced by the state of the SiO_2 surface. The lower limit depends more on the O_2 pressure than on any other single factor. F. L. U.

Ignition of gaseous mixtures by the corona discharge. R. W. Sloane (Phil. Mag., 1935, [vii], **19**, 998—1011).—A coal gas–air mixture (I) could not be ignited by discharges between electrodes of cold glass, ebonite, or paraffin wax, but white fibre, glass at 100°, or slate was effective. The variation of the least igniting % of coal gas with electrode temp. and conductivity has been determined, and igniting energies calc. Igniting currents are given for the steady corona discharge between slate electrodes in the most easily ignited (I). R. S.

Highly-attenuated flames of potassium and iodine vapours. E. Roth and G. Schay (Z. physikal. Chem., 1935, **B**, **28**, 323—331).—These are essentially similar to $K+Cl_2$ and $K+Br_2$ flames (cf. A., 1933, 206). One of the differences is that the energy of the secondary gas reaction, $K_2+I=KI+K$, is insufficient to excite the violet K doublet, and therefore both the first stage of the reaction, $K+I_2=KI+I$, and the second, $K+I=KI$, excite only the red doublet. From the distribution of the KI formed and the variation of light yield with pressure and temp. the velocity coeffs. of the various reactions have been calc. The heat of dissociation of K_2 is calc. to be 18·7 kg.-cal. The mechanism previously suggested for the continuous light emission must be rejected; it must be supposed instead that a highly excited K atom is formed from a K ion and an electron and remains for a relatively long time in excited states, the excess energy being radiated away in a continuous manner by interaction with a K atom. R. C.

Highly-attenuated flames of potassium and mercuric chloride vapours. I. Berger and G. Schay (Z. physikal. Chem., 1935, **B**, **28**, 332—339).—The mechanism is completely analogous to that of $Na+HgCl_2$ flames: $K+HgCl_2=KCl+HgCl$, $K+HgCl=KCl+Hg$ (cf. A., 1928, 1339). The second stage is responsible for the emission of the red and violet K doublets, whilst the first causes no light emission. Both red and violet emission exhibit the characteristics of flame type II. The emission of the red doublet is by primary excitation of the 3^2D level, not direct. There is an intense bluish glow on the wall, due to reaction of $HgCl_2$ mols. with K vapour there. A second wall reaction occurs between HgCl radicals and K vapour, and is responsible for the electrical conductivity of the flame and the continuous emission. R. C.

Thermal decomposition of acetaldehyde and propaldehyde. F. Patat and H. Sachsse (Naturwiss., 1935, **23**, 247—248).—The theory of Rice and Herzfeld (A., 1934, 369) that the thermal decomp. of MeCHO involves the formation of free radicals, with a subsequent chain mechanism, is disproved by the fact that [H] during the decomp. is $< 4\times10^{-13}$ g.-mol. per litre. To bring this result into agreement with a chain mechanism would require a heat of activation of 29,000 g.-cal. for the reaction $CH_3+H_2=CH_4+H$, which is too high. Similar results were obtained with EtCHO. A. J. M.

Thermal decomposition of acetaldehyde. M. W. Travers (Nature, 1935, **135**, 511). L. S. T.

Critical phenomena in the oxidation and self-inflammation of hydrocarbons. M. Neumann and B. Aivazov (Nature, 1935, **135**, 655—656).—The velocity of oxidation of C_5H_{12} in $C_5H_{12}+8O_2$ mixtures has been studied in quartz vessels at various pressures below the ignition limit over a temp. range 300—500°. At low temp. there is a rapid reaction, accompanied by chemiluminescence, after a fairly long induction period. The rate of reaction increases rapidly with a rise in temp. up to a max. at approx. 340°. From 350° to 500° increase is slow and after 500°, rapid. With increasing pressure two regions of thermal ignition at low, approx. 300°, and at high, approx. 500°, temp. are thus to be expected. The results support the view that in addition to the direct oxidation there is a catalytic reaction involved. L. S. T.

Thermal decomposition of nitrosyl chloride. G. Waddington and R. C. Tolman (J. Amer. Chem.

Soc., 1935, 57, 689—692).—The homogeneous reaction between 150·1° and 250·7° is a bimol. decomp. accompanied by a termol. reverse reaction. When the energy of activation is expressed in g.-cal., the sp. rate const. as a function of temp. for the decomp. reaction is given by $k=4\cdot3\times10^{11}T^{\frac{1}{2}}e^{-24,000R/T}$ c.c. mol.$^{-1}$ sec.$^{-1}$ E. S. H.

Dependence of methane–oxygen low-pressure explosion limit on nature of reaction vessel surface. H. H. Storch (J. Amer. Chem. Soc., 1935, 57, 685—686).—The limiting pressures vary widely with the treatment of the quartz surface of the reaction vessel. E. S. H.

Chemical kinetics of the reaction of oxygen with hydrogen and with deuterium. L. S. Kassel and H. H. Storch (J. Amer. Chem. Soc., 1935, 57, 672—678).—Theoretical. The theory of chain reactions for which the chains are broken at the wall at only a fraction of the total no. of collisions is developed and shown to differ from the case where every collision leads to destruction. The possible chain mechanisms for the explosion limits of H_2–O_2 have been investigated. Published experiments involving D_2 are analysed. E. S. H.

Kinetics of the reaction between oxyhalogen and halogen acids. J. Hirade (Bull. Chem. Soc. Japan, 1935, 10, 97—121).—The following reactions have been studied in the presence of neutral salts and also of other acids: $HClO_3$ with HCl and HBr, $HBrO_3$ with HCl, and HIO_3 with HCl and HBr. The reaction velocity is expressed by the formula $-d(XO_3')/dt=kF(XO_3')^x(Y')^y(H^·)^z$, where F is Brönsted's kinetic activity factor and x, y, and z are 1, 1, and 2 for reactions $HClO_3$–HY, $HBrO_3$–HBr, and HIO_3–HI, 1, 2, 2 for $HBrO_3$–HCl and $HBrO_3$–HI, 1, 4, 4 for HIO_3–HCl, and 1, 2, 3 for HIO_3–HBr. The velocity coeffs. for the reduction of any one HXO_3 are in the order HI>HBr>HCl, following the order of the reduction potentials, and for the oxidation of any one HY, HIO_3>$HBrO_3$>$HClO_3$, with the single exception of the reaction HIO_3–HCl which takes place with difficulty. The primary process of the $HClO_3$–HCl reaction is $ClO_3'+Cl'+2H^·=HClO_3+HCl \rightleftharpoons HClO_2+HClO$. Several secondary reactions occur to a varying extent, depending on conditions. Reaction mechanisms are also suggested for the other pairs of reactants. M. S. B.

Velocity of saponification of some simple triglycerides by ethyl-alcoholic potash. P. E. Verkade and A. H. A. de Willigen (Rec. trav. chim., 1935, 54, 353—357).—The velocity coeffs. of saponification by EtOH–KOH of trioctoin, trinonoin, tridecoin, triundecoin, trilaurin, and tritridecoin are the same at 37·5°. The triglycerides form Et esters of the glyceride acid with EtOH very rapidly in presence of KOH, and these esters are saponified at the same rate. R. S. B.

Neutral salt action of the reaction between acetylglycollate and hydroxyl ions in dilute solution. A. von Kiss (Rec. trav. chim., 1935, 54, 337—344).—In presence of $Li^·$, $Na^·$, and $K^·$ (as hydroxides) at ionic strengths (μ) 0·0014—0·03 the reaction between $OAc·CH_2·CO_2'$ and OH' at 0·0007—0·02M at 25° follows the simple Brönsted–Debye–Hückel formula (a), but there is a sp. action for each alkali metal ion, even at μ=0·0014. $Ca^{··}$, $Sr^{··}$, and $Ba^{··}$, μ=0·0021—0·045, disagree with (a) and with the formula corr. for ionic size (b). With $\mu>0\cdot03$ $Li^·$, $Na^·$, and $K^·$ agree with (b). On account of the sp. action of ions mixtures of hydroxides and salts give reaction coeffs. which do not agree with (a) and (b). R. S. B.

Carbon dioxide cleavage from dibromomalonic acid. (Miss) J. Muus (J. Physical Chem., 1935, 39, 343—353).—The velocity of the reaction $CBr_2(CO_2H)_2 \longrightarrow CHBr_2·CO_2H+CO_2$ has been determined at 25° for different p_H and different salt concns. At const. p_H the reaction is unimol. Concn. dissociation consts. of $CBr_2(CO_2H)_2$, determined electrometrically for salt concns. 0·1, 0·2, and 1·0N, are K_1 1 and K_2 $9\cdot0\times10^{-3}$, $1\cdot5\times10^{-2}$, and $1\cdot70\times10^{-2}$, respectively. The results are in agreement with the assumption that the reaction is due to the spontaneous decomp. of $CBr_2(CO_2H)·CO_2'$. The temp. coeff. is 4·01, giving an energy of activation of 25,000 g.-cal. The following concn. dissociation consts. have also been determined at 25°: glycine in 0·2N-salt $4\cdot68\times10^{-3}$, citric acid in N-salt K_1 $1\cdot71\times10^{-3}$, K_2 $8\cdot05\times10^{-5}$, AcOH in N-salt $2\cdot95\times10^{-5}$. M. S. B.

Fission of carbon chains. Thermal decomposition of hydrocarbons.—See this vol., 727.

Relationships between affinity and velocity of reaction. J. R. Velasco (Anal. Fís. Quím., 1935, 32, 345—369).—Measurements of the velocity of reaction between diphenylsemicarbazide and toluquinone, benzoquinone, 2 : 6-dichlorobenzoquinone, and tolylsulphoquinone in glacial AcOH at 20°, 30°, and 40° indicate that $\log k_2/k_1=16\cdot14(E_2-E_1)$, where k_1 and k_2 are the velocity coeffs. and E_1 and E_2 are the oxidation potentials for two different quinones. D. R. D.

Temperature increment of reaction velocity in reactions of type $A_{solid}=B_{solid}+C_{gas}$. J. Zawadzki and S. Bretsnajder (Z. Elektrochem., 1935, 41, 215—223; cf. A., 1933, 911).—The velocity of decomp. of $CaCO_3$ (calcite) has been measured over the range 690—840° both in a vac. and at const. pressure. The temp. increment of the velocity=heat of reaction. Attention is directed to the similarity of condensation and vaporisation processes to combination and decomp. in reactions of the above type, with respect to rate of formation of nuclei and to temp. relations. F. L. U.

Kinetics of the electrochemical chlorination of benzene. W. Jeunehomme (J. Chim. phys., 1935, 32, 173—198).—PhCl and H are the primary products of electrolysis of HCl in MeOH containing C_6H_6. The chlorination proceeds partly by the homogeneous reaction of free dissolved Cl_2 with C_6H_6 near the anode and partly by direct reaction of Cl and C_6H_6 on the anode surface. In the former reaction the disappearance of Cl_2 follows a simple unimol. law and is accelerated by HCl; at low [HCl] MeOH is attacked rather than C_6H_6. On the electrode surface (bright Pt) the proportion of Cl atoms reacting directly with

C_6H_6 mols. is equal to the proportion by vol. of C_6H_6 in the liquid and the rate is independent of [HCl]. D. R. D.

Apparent rates of oxidation of massicot and litharge. K. C. CHANG and Y. F. SU (J. Chinese Chem. Soc., 1935, **3**, 86—94).—Differential equations representing the course of the reaction and the reaction const. at various temp. between 350° and 500° have been determined for the oxidation of the two forms of PbO. J. W. S.

Ageing of ferric orthohydroxide, and its conversion into α-FeO_2H as a phenomenon of discontinuous crystallisation or devitrification. A. KRAUSE [with W. ŚWIATKOWSKA, H. TORNO, and J. STOCKÓWNA] (Rocz. Chem., 1935, **15**, 15—25).—Determinations of the velocity of transformation of *o*-$Fe(OH)_3$ (I) into goethite (II) indicate that the process depends on formation of nuclei of amorphous cyclic polyferrous acids, which then undergo crystallisation with the production of (II). (I) gels are the most stable at the isoelectric point. R. T.

Hydrolysis of secondary and tertiary alkyl halides. E. D. HUGHES (J. Amer. Chem. Soc., 1935, **57**, 708—709).—Hydrolysis of Me and Et halides by dil. aq. EtOH–KOH is unimol., that of $Pr^{\beta}Br$, $Bu^{\beta}Br$, and CMe_2EtBr bimol. The theory of Ingold *et al.* (A., 1933, 701) is applied to these and other results. R. S. C.

Reactivity and constitution of nitric and sulphuric acids. V. Sulphonating action of sulphuric acid in aqueous and acetic solutions. VI. Viscosity, electrical conductivity, and Raman spectrum of mixtures of sulphuric and acetic acids. E. BRINER, J. W. HOEKSTRA, and B. SUSZ (Helv. Chim. Acta, 1935, **18**, 684—693, 693—700; cf. this vol., 564).—V. The velocity of sulphonation of PhOH is greater in AcOH than in H_2O; the temp. coeff. is greater in H_2O. The influence of concn. has also been studied. The facts suggest that non-dissociated H_2SO_4 is the sulphonating agent.

VI. The variation of properties with composition indicates the existence of H_2SO_4,AcOH. E. S. H.

Hydrolysis of ethyl iodide. J. GREENSPAN, S. LIOTTA, and V. K. LA MER (Trans. Faraday Soc., 1935, **31**, 824—825).—Hydrolysis of EtI by dil. aq. NaOH proceeds normally and quantitatively. Results reported by Moelwyn-Hughes (A., 1934, 152) are incorrect. F. L. U.

Catalytic effect of hydrogen on the carbon monoxide flame. B. W. BRADFORD (Chem. and Ind., 1935, 469; cf. A., 1934, 145).—A reply (cf. this vol., 588). The walls did not have an appreciable differential effect on the flame reactions. J. G. A. G.

Mechanism of aromatic side-chain reactions with special reference to the polar effects of substituents. III. Effect of unipolar substituents on the critical energy and probability factors in the interaction of benzyl bromide with pyridine and α-picoline in various solvents. J. W. BAKER and W. S. NATHAN (J.C.S., 1935, 519—527; cf. A., 1934, 970).—The supposed catalysis by salts (*loc. cit.*) is due to the equilibrium $ArBr+ArC_5H_5\overset{\oplus}{N}\}\overset{\ominus}{N}O_3 \rightleftharpoons ArO{\cdot}NO_2+ArC_5H_5\overset{\oplus}{N}\}\overset{\ominus}{Br}$, and benzylpyridinium bromide catalyses slightly the reaction between CH_2PhBr and C_5H_5N in dry $COMe_2$ (I). From velocity measurements at 0—40°, the energy of activation of the reaction of *p*-R·C_6H_4·CH_2Br (R=H, Me, NO_2) with C_5H_5N (II) and α-picoline (III) is 11·9—12·48 kg.-cal. in (I), 13·68—13·84 in aq. 90% $COMe_2$ (IV), and 15·3—16·0 in aq. 90% EtOH (V). The probability factors ($\times 10^6$) are 0·047—0·139 with (III) and 0·515—0·87 with (II) in (I), 11·7—23·17 with (II) in (IV), and 91·3—836·7 with (II) in (V). These results are discussed with reference to the mechanism in ionising and non-ionising media. J. G. A. G.

Exchange between ammonia and deuterium on catalytic iron surfaces. H. S. TAYLOR and J. C. JUNGERS (J. Amer. Chem. Soc., 1935, **57**, 660—661).—The exchange occurs at an Fe–K_2O–Al_2O_3 catalyst at room temp., but not at fused quartz surfaces even at 300°. The bearing on the problem of kinetics of NH_3 synthesis is discussed. E. S. H.

Exchange reactions between heavy hydrogen and hydrogen adsorbed in solids. A. FARKAS and L. FARKAS (Trans. Faraday Soc., 1935, **31**, 821—824).—At temp. > 600° D_2 can undergo an exchange reaction with H_2 sorbed in SiO_2 or Pt even when these materials have been thoroughly outgassed in a high vac. Attention is directed to possible consequences of this effect. F. L. U.

Hydrogen catalysis on nickel. I Comparison of rates of para-hydrogen transformation and $H_2+D_2=2HD$ on nickel. II. Sintering experiments. E. FAJANS (Z. physikal. Chem., 1935, B, **28**, 239—251, 252—256).—I. Change in gas temp. at const. catalyst temp. affects the rate of the *p*-H_2 transformation (I) on Ni only to the extent that it alters the collision no. Comparing the effect of temp. on (I) and $H_2+D_2=2HD$ (II) shows the heat of activation of (II) to be the greater by ~1410 g.-cal. The apparent order of both reactions is approx. the same (~0·7) and at 14° the ratio of the velocity coeff. of (I) to that of (II) is approx. const. at ~3 for catalysts of widely varying activity. It is concluded that both reactions have the same mechanism, involving passage through the at. state (III). The transition into (III) possibly requires a heat of activation, which for D_2 is > for H_2 owing to the smaller zero point energy.

II. The sintering of the catalyst for (I) begins at temp. which are the lower the higher is its activity, *A*. In sintering at a given temp. *A* reaches a const. val. after the first ten min., which is independent of the initial *A*, but varies with the temp., *i.e.*, with every sintering temp. corresponds a definite state of surface activity. The catalyst is reversibly poisoned when heated in H_2. R. C.

Decomposition of deutero-ammonia on tungsten filaments. J. C. JUNGERS and H. S. TAYLOR (J. Amer. Chem. Soc., 1935, **57**, 679—681).—The decomp. at about 950° abs. and 3·5—15 cm. is an approx. zero-order reaction, which is slower than that of NH_3 under the same conditions in the ratio 1 : 1·6. The decrease in rate of decomp. in mixed ammonias

∝ the D content. The temp. coeffs. of NH_3 and ND_3 are the same. E. S. H.

Polymerisation of formaldehyde. J. E. Carruthers and R. G. W. Norrish (Nature, 1935, **135**, 582—583).—Small amounts of HCO_2H (I) and of AcOH accelerate the polymerisation of CH_2O. With (I) the reaction is approx. unimol. and the rate is practically unaffected by packing the vessel with quartz tubes. (I) is not appreciably consumed. The polymerisation thus induced by (I) is regarded as a chain mechanism in which the starting of reaction chains and also the branching are controlled kinetically by (I). With MeCHO vapour at room temp. a similar polymerisation is induced by (I). L. S. T.

Application of catalytic reactions in qualitative and quantitative microanalysis. R. Lucas and F. Grassner (Mikrochem., 1935, **17**, 237—261).—A review.

Adsorption and catalysis. M. Polanyi (J.S.C.I., 1935, **54**, 123—124T).—The energy relationships necessary for surface catalysis are discussed, with special reference to $H_2+D_2 \longrightarrow 2HD$. The most active catalytic surfaces for the H interchange are those in which the H–metal linking is of the order of 50,000 g.-cal. Metals are therefore divided into two groups: those in which the surface valencies are respectively weaker than 50,000 g.-cal. (slow catalysts) and about 50,000 g.-cal. (good catalysts). The possibility of catalytic reactions occurring by a dissolution process of the H in the at. state in the surface layers of the metal is discussed. Contrary to the various theories on activated adsorption, catalytic activity should not be a strong, but an extremely weak, adsorption.

Surface reactions at very low pressures. I. Platinum–chlorine. A. Processes on the surface of the metal in the form of filament. C. Nogareda (Anal. Fís. Quím., 1934, **32**, 286—344).—Cl_2 at approx. 10^{-6} mm. pressure was brought in contact with a heated Pt filament in an ice-cooled vessel. Examination of the velocity of the reaction and nature of the products indicates that at 600—900° the simple second-order reaction $Pt+2Cl_2 \longrightarrow PtCl_4$ occurs and adsorption is absent. At 1200°, adsorption of at. Cl takes place, followed by the zero-order reaction $Pt+2Cl$ (adsorbed) $\longrightarrow PtCl_2$, the $PtCl_2$ being subsequently oxidised to $PtCl_4$ (first-order reaction). D. R. D.

Catalytic activities of nickel–copper catalysts. K. Yoshikawa (Bull. Inst. Phys. Chem. Res. Japan, 1935, **14**, 308—312).—Ni and Ni–Cu catalysts have been progressively poisoned by thiophen. The no. of highly reactive centres is diminished by the addition of Cu to Ni, whilst the no. of moderately active centres and the total surface available for reaction are increased. R. S.

Heterogeneous catalysis in gas reactions, reactions between gases and non-gaseous substances, and the poisoning of catalysts. M. Pourbaix (Bull. Soc. Belge Ing. Ind., 1934, No. 7—8, 67 pp.; Chem. Zentr., 1934, ii, 3586—3587).—A review and discussion. H. J. E.

Catalytic decomposition of acetaldehyde. M. S. Ebert (J. Physical Chem., 1935, **39**, 421—424).—Of many catalysts examined, Ni, obtained by pptg. aq. $Ni(NO_3)_2$ with NaOH and reducing at 400°, was found to be the most satisfactory for the reaction $MeCHO \longrightarrow CO+CH_4$ at 175—225°. Equilibrium conditions appear to be obtained, but attempts to reach them by synthesis were unsuccessful. M. S. B.

Activity of chromium catalysts.—See B., 1935, 403.

Hydrogenation catalysts.—See B., 1935, 403.

Activity of mixed catalysts in the simultaneous dehydration of ethyl alcohol and ammonia.—See this vol., 742.

Causes of increase in activity of platinum gauze in the oxidation of ammonia.—See B., 1935, 402.

[Catalytic] hydrogenation of acetylene.—See B., 1935, 394.

[Catalytic] transformation of carbon monoxide and carbon dioxide into methane at high pressure.—See B., 1935, 390.

Catalytic oxidation of methyl alcohol to formaldehyde.—See B., 1935, 442.

Autoxidation of α-pinene.—See this vol., 754.

Concentration of tritium (H^3). P. W. Selwood, H. S. Taylor, W. W. Lozier, and W. Bleakney (J. Amer. Chem. Soc., 1935, **57**, 780).—The concn. of H^3 has been increased to 1 in 10^4 by electrolysing 75 metric tons of H_2O down to 0·5 c.c. The abundance of H^3 in H_2O is 7 in 10^{10}. E. S. H.

Electrolytic concentration of oxygen isotopes. P. W. Selwood, H. S. Taylor, J. A. Hipple, jun., and W. Bleakney (J. Amer. Chem. Soc., 1935, **57**, 642—644).—The concn. of O^{18} was increased only 10% by electrolysing 117 litres of H_2O down to 1 c.c. The ratio of sp. rates of discharge of O^{16} and O^{18} is 1·01. E. S. H.

Electrodeposition of (A) niobium, (B) tantalum. N. A. Isgarischev (J. Gen. Chem. Russ., 1934, **4**, 1415—1421, 1422—1427).—(A) [with G. E. Kaplan]. During electrolysis of solutions containing Nb and Ta, part of the Nb is deposited as a bright, adherent coating on the cathode, an equal amount undergoes pptn. from the electrolyte, whilst the greater part is converted into a non-electrolytic form, not pptd. by tannin. Ta is not deposited.

(B) [with A. F. Prede]. Ta is electrodeposited on Cu cathodes from solutions at 70—80°, containing 50% of resorcinol (I); deposition commences 1 hr. after passage of current, and does not take place when the anolyte and catholyte are separated by a diaphragm, pointing to the existence of a preparatory process in the anolyte. Satisfactory deposition is not obtained when a no. of other substances are substituted for (I). R. T.

Metallic gadolinium. F. Trombe (Bull. Soc. chim., 1935, [v], **2**, 660—664).—A button of pure Gd (Si 0·7, Fe 0·3%) was obtained by electrolysing a bath containing $GdCl_3$ 45, KCl 44, and LiCl 12% at

625—675° in a C crucible (serving as anode), using molten Cd (in a CaF_2 cup) as cathode, and distilling off the Cd from the resultant alloy in vac. (< 0·001 mm.) at 450—1240°. D. R. D.

Electro-deposition of chromium from chromic acid solutions.—See B., 1935, 413.

Oxidation of sulphur dioxide in a high-voltage arc discharge. L. A. Kolodkina and N. N. Nechaeva (J. Phys. Chem. U.S.S.R., 1933, **4**, 845—853).—For the same power output more SO_3 is obtained at higher c.d. Decreasing the gas velocity or $[SO_2]$ in the SO_2+air mixture increases the yield to 95—98% at low velocities and $[SO_2]$. Voltages from 9·5 to 34 kv. were used. For practical purposes 65—70% oxidation is possible. Ch. Abs. (*e*)

Oxidation of sulphur dioxide in a high-frequency discharge. N. Zalogin and N. Nechaeva (J. Phys. Chem. U.S.S.R., 1933, **4**, 832—844).—The total O_3 yield increased with the velocity of the air stream, but the % yield decreased linearly. The yield of SO_3 (I) from SO_2 decreased linearly with increasing $[SO_2]$ in the gas mixture, and velocity of gas stream. Increasing H_2O vapour concn. increased (I) as an S-curve function. Glycerol and EtOH were used to stabilise the standard aq. Na_2SO_3 used for O_3 analysis. Ch. Abs. (*e*)

Relation between p_H and photographic sensitivity. A. Steigmann (Phot. Ind., 1934, **32**, 93).—The increased sensitivity of emulsions with an alkaline reaction is attributed (1) to complexes from the natural sensitisers of the gelatin (I) and the Ag halides yielding Ag_2S only in an alkaline medium; (2) to the decrease in protective action of (I) at p_H 7—8·9 compared with p_H 5—6·5, which facilitates ripening. Ch. Abs. (*e*)

[Photographic] density surfaces by physical development. H. Arens (Z. wiss. Phot., 1935, **33**, 281—286).—Densities are shown as contour lines (by projection) on log *I*–log *t* graphs, for fine-grain slow emulsions with chemical and with physical development, and for a large-grain emulsion by physical development; the only differences are those of degree. For log $I > 0$, solarisation is found when proceeding along the time axis, but not when proceeding along a light-intensity axis for a given log *t* val. J. L.

Photographic development. W. Meidinger (Physikal. Z., 1935, **36**, 312—320).—The kinetics of development of a very slow AgBr–gelatin emulsion (without AgI) with a metol–quinol developer containing excess of KBr has been investigated. The mean time for reduction of a nucleus over the whole range of the blackening curve, including solarisation, is independent of the length of exposure. The process of development depends on (*a*) the probability of the commencement of development, and (*b*) the reduction time. (*b*) is independent of length of exposure if conditions of development are the same. The effect of solarisation (I) is due to a decrease in (*a*), and not an increase in (*b*). The decrease in (I) due to NO_2' is due to increase in (*a*). The method might be employed to determine the distribution of the Ag particles in their primary separation from the nuclei, and the structure of the blackening curve for physical development. A. J. M.

Influence of cations on the sensitivity of photographic emulsions. A. Charriou and (Mlle.) S. Valette (Compt. rend., 1935, **200**, 1189—1191).—The sensitivity (I) of a photographic emulsion (AgI : AgBr=0·0465) is unaffected by Cd, Al, or Mg. Mg diminishes the rate of formation of chemical fog (II). (I) and (II) are decreased by Th, $Fe^{\cdot\cdot\cdot}$, Zr, As, Pb, Co, and Cu, in increasing order of efficiency; (I) is decreased and (II) increased by Tl, NO_2, Au, Ni, $Fe^{\cdot\cdot}$, and $Hg^{\cdot\cdot}$. $Hg^{\cdot}$, very low concns. of $Fe^{\cdot\cdot}$, and Ag increase (I). Ag also increases (II). J. W. S.

Pressure effect on photographic sensitivity. N. T. Zé and T. L. Chao (Chinese J. Physics, 1934, **1**, 66—75).—Pressures (*p*) of 0—1250 kg. per sq. cm. reduce the photographic sensitivity in the region of normal and over-exposure, and of reversal. For $p > 200$ kg. per sq. cm. $E_p/E = a + \alpha p$, where *E* is the illumination required to produce the same optical density without pressure as that obtained when the illumination E_p is used with pressure, and *a* and α are consts. The influence of *p* decreases with λ; with the same λ *a* and α vary greatly with the type of film. Applications are discussed. R. S. B.

Ascorbic acid (vitamin-*C*) and photographic developing action. C. E. Bills (Science, 1935, **81**, 257—258).—Ascorbic acid (I) in aq. Na_2SO_3 and aq. Na_2CO_3 is a rapid developer which produces a black image and considerable fog. The addition of 20 mg. of KBr per litre restrains fog, retards development, and changes the colour of the image from black to brown. The action on various photographic papers is described. The bearing of the developing action of (I) on the theory relating developing function to mol. configuration is discussed. L. S. T.

Influence of alkali iodides on the properties of photographic emulsions. A. Charriou and (Mlle.) S. Valette (Compt. rend., 1935, **200**, 916—918; cf. B., 1933, 333).—With increasing [I′] the sensitivity of a photographic emulsion (I) first decreases, passes through a min., and then increases. The greater is [AgI] in (I) the less is the initial fall with addition of I′ and the greater is the increase of sensitivity with increasing [I′] after the min. Increasing [I′] also causes increasing tendency for solarisation up to the concn. which yields min. sensitivity, further additions decreasing this tendency. The observations invalidate the theories which attribute the deactivating properties of halides to halogenation of particles of Ag liberated by reduction of AgBr during prep. of (I). J. W. S.

Decomposition of silver–gelatin complex and its significance for the light-sensitivity [of photographic emulsions]. W. Schleussner (Z. wiss. Phot., 1935, **34**, 63—71).—Ag ions form a complex with gelatin (Ag gelatinate) which decomposes in the warm to form a stabler complex (I) ("primary Ag") which is not decomposed by KCN. The rate of formation of (I) (in presence of a very little AgBr in a $AgNO_3$–gelatin emulsion, a max. is reached in 5 hr.) is similar to the growth of sensitivity to light

and of fog developable in metol. Quinol gives no fog, small nuclei only being developed. The action of light appears to be the formation of large nuclei from (I), by liberation and wandering of electrons. J. L.

Artificial photographic light sources. O. Reeb (Z. wiss. Phot., 1935, **34**, 77—87).—Various kinds of continuous light and short-emission sources are discussed and compared with regard to colour temp. and energy distribution and actinic val. J. L.

Ultra-violet photolysis of fructose in pure and aqueous glycerol. R. Cantieni (Helv. Chim. Acta, 1935, **18**, 473—475).—Fructose in glycerol solution is decomposed by ultra-violet light with evolution of gas. With increasing addition of H_2O the rate of decomp. increases. E. S. H.

Effect of temperature on the photochemical decomposition of acetone. C. A. Winkler (Trans. Faraday Soc., 1935, **31**, 761—765).—The quantum efficiency in the decomp. of $COMe_2$ over the range 2200—3300 Å. is five times as great at 100° as it is at 60°, and maintains the higher val. up to 400°. The influence of temp. on the rate of decomp. is much greater for higher than for lower λ. It is suggested that the efficiency increases with rise of temp. more rapidly for quanta of small than of large energy content, owing to the greater importance of the thermal contribution in the former case. F. L. U.

Internal light filters. Effect of azo-dyes on the photolysis of diazo-compounds. M. Horio and S. Yamashita (Z. wiss. Phot., 1935, **33**, 273—280).—The photolysis of *p*-diazodiphenylamine sulphate and of 1 : 2 : 4-diazonaphtholsulphonic acid in aq. solutions, in the presence of varying amounts of Crystal-scarlet 6 RA extra, and of Orange II, has been studied by measurement of the absorption and the extinction coeffs. The source of light was a filtered Hg-vapour lamp, giving the lines 4360 and 4050 Å. The velocities of decomp. found agree with those calc. from the Luther–Weigert–Langendijk formulæ. J. L.

Primary photochemical reactions. VI. Photochemical decomposition of cyclic ketones. (Miss) O. D. Saltmarsh and R. G. W. Norrish (J.C.S., 1935, 455—459).—*cyclo*-Heptanone (I), -hexanone (II) and -pentanone (III) absorb light of λ 3500—2000 Å., and in the full radiation of the Hg lamp the decomps. of the vapours are: (1) (I)⟶ *cyclo*hexane+CO (80—95%) accompanied by (I)⟶ $2C_3H_6$+CO (4%), (2) (II)⟶*cyclo*pentane+CO (92%) accompanied by (I)⟶$C_2H_4+C_3H_6$+CO (8%), and (3) (III)⟶$2C_2H_4$+CO (50%) with (III)⟶C_4H_8+CO (50%). The CO is eliminated by the almost simultaneous rupture of the two linkings uniting it to the ring and, since the changes are either exothermic or thermo-neutral, it is suggested that the vibrations of the resulting cyclic hydrocarbon lead to slight decomp. in cases (1) and (2) and complete decomp. or isomerisation in case (3). J. G. A. G.

Relations between the optical properties of the medium and the photochemical constants of tetraphenylrubene. C. Dufraisse and M. Badoche (Compt. rend., 1935, **200**, 1103—1105).—The relative rates of photochemical oxidation of tetraphenylrubene have been determined in different solvents and compared with the variations in the position of max. absorption (I). In general the oxidation is more rapid the nearer (I) approaches the red, but no definite relations can be deduced. The behaviour of mixtures of solvents has also been studied. The positive activity of CS_2 is strongly diminished by Et_2O, but the negative activity of $PhNO_2$ is not affected by dilution. M. S. B.

Photosynthesis of formaldehyde in tropical sunlight. V. Gore (J. Physical Chem., 1935, **39**, 399—402).—The photo-reduction of nascent CO_2 to form CH_2O requires the presence of nascent H. An apparatus for exposing CO_2 and H_2 to light is described; the use of corks, rubber tubing, and taps is avoided. The impurities usually present in CO_2 prepared from marble and HCl are probably H_2S and SO_2. M. S. B.

Photographic emulsions.—See B., 1935, 525.

Origin of the luminosity which accompanies the detonation of explosives. H. Muraour and A. Michel-Lévy (Compt. rend., 1935, **200**, 924—926).—It is suggested that on the passage of a sufficiently powerful detonation wave the gas surrounding the explosive is compressed adiabatically, and hence is heated to a high temp. and becomes luminous. The fact that the luminosity does not disappear immediately is attributed to the formation of active gas, of which the luminosity decreases progressively. J. W. S.

Chemical decomposition of silver oxide by slow electrons. P. H. Wei, P. A. Anderson, and Y. M. Hsieh (J. Chinese Chem. Soc., 1935, **3**, 6—15).—No increase in conductivity could be observed > the increase due to ageing in a vac., when a thin film of Ag_2O was bombarded with an intense beam of electrons of up to 108 e.v. Explanations are suggested for the apparent non-reduction of the Ag_2O. J. W. S.

Applications of deuterium. F. G. Brickwedde (J. Washington Acad. Sci., 1935, **25**, 157—166).—A review of published work, mainly on the study of mechanism of reactions by exchange between D and H. E. S. H.

Alleged isotopic interchange between water and acetylene. R. P. Bell (J. Amer. Chem. Soc., 1935, **57**, 778—779).—Recent work (A., 1934, 853) has not been confirmed. E. S. H.

Isotopic interchange between acetylene and heavy water. L. H. Reyerson (J. Amer. Chem. Soc., 1935, **57**, 779—780).—A reply (cf. preceding abstract). E. S. H.

Action of molten lithium salts on glass. O. J. Stewart and D. W. Young (J. Amer. Chem. Soc., 1935, **57**, 695—698).—When soda-glass is immersed in molten $LiNO_3$ exchange occurs between Na and Li. E. S. H.

Hydrolysis of alkali hydrides and the nature of the chemical linking between hydrogen and strongly electropositive metals. J. Henrion (Bull. Soc. chim. Belg., 1935, **44**, 210—213).—Consistent with the theory that H_2 mols. are the

initial product of the hydrolysis of alkali hydrides, carefully purified NaH, KH, and CaH_2 do not decolorise aq. safranine-*T*. J. G. A. G.

Pure cuprous oxide for deducing the law of multiple proportions. R. SCHARF (Z. physik. chem. Unterr., 1934, **47**, 202—204; Chem. Zentr., 1934, ii, 3581).—Pure Cu_2O is prepared by heating equiv. quantities of Cu and CuO to a red heat in absence of air. H. J. E.

Copper tetramminosulphate. I. Preparation, analysis, and preservation. P. G. PATERNOSTO and E. DEL CARLO (Rev. fac. cienc. quim., La Plata, 1934, **9**, 7—14).—$Cu(NH_3)_4SO_4,H_2O$, prepared and dried by the methods described, is stable in closed vessels. When heated in air it loses NH_3 and H_2O, but its composition remains unaltered after heating in sealed vessels to 250°. Aq. solutions $< 0{\cdot}05M$ hydrolyse immediately, pptg. basic Cu salts. More conc. solutions, or solutions to which NH_4 salts have been added, hydrolyse more slowly. F. A. A.

Production of magnesium and potassium chlorates. F. BRIERS (School Sci. Rev., 1934, **16**, 277).—MgO is treated with Cl_2 to give $MgCl_2$ and $Mg(ClO_3)_2$. The latter is metathesised with KCl. Anhyd. $MgCl_2$ is electrolysed with gas-C anodes and molten Pb cathode. Mg is recovered from the resulting Mg–Pb alloy by making the alloy the anode in a fused $MgCl_2$ electrolyte and adjusting the current so that no Cl_2 is liberated. CH. ABS. (*e*)

Synthetic spinels coloured with cobalt. H. W. TROMNAU (Jahrb. Min., 1934, **A**, **68**, 349—376; Chem. Zentr., 1934, ii, 3740).—The probable composition is MgO,xAl_2O_3 and $CoAl_2O_4$, *d* increasing and hardness decreasing with increasing [Co]. The optical properties are described. H. J. E.

Reduction of alkaline-earth arsenates by carbon. Tristrontium and tricalcium arsenates. H. GUÉRIN (Compt. rend., 1935, **200**, 1210—1212; cf. this vol., 313).—$Ca_3(AsO_4)_2$ and $Sr_3(AsO_4)_2$ are reduced by C, slowly at 800° and rapidly at 850°, yielding first the arsenites and finally As and SrO or CaO. Rapid heating to 1500—1600° yields Ca_3As_2 and Sr_3As_2. If the heating is slow loss of As occurs. J. W. S.

Exchange reactions between finely-divided crystalline phases and gases. E. HERTEL and H. VON HOLT (Z. physikal. Chem., 1935, **B**, **28**, 393—401).—Basic Zn chromate decomposes above 400° into $ZnCr_2O_4$ (spinel lattice), ZnO (zincite lattice), and O_2. $ZnCr_2O_4$ reacts with dry H_2S at 450—500°, $ZnCr_2O_4+4H_2S=ZnCr_2S_4+4H_2O$, the spinel lattice being retained, but somewhat distended; similarly ZnO yields wurtzite (I). Steam at 480° largely reconverts $ZnCr_2S_4$ into $ZnCrO_4$, but a little Cr sulphide is formed, which gives Cr_2O_3 on heating in air. (I) cannot be reconverted into ZnO by steam at 500°; O_2 is required. Dry H_2S at 450—500° converts Cr_2O_3 into amorphous Cr_2S_3. R. C.

Complex salts of 2 : 2′-dipyridyl with zinc and cadmium. II. F. M. JAEGER and J. A. VAN DIJK (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 235—242; cf. this vol., 312).—The following *salts* have been prepared from 2 : 2′-dipyridyl (dipy): $[Zn\ dipy(H_2O)_2](NO_3)_2,H_2O$, $[Zn\ (dipy)_3](NO_3)_2,6H_2O$, $[Cd\ dipy(H_2O)_2]SO_4,2H_2O$, $[Cd\ (dipy)_3]SO_4,3H_2O$, $[Cd\ dipyCl_2]$, and $[Cd\ (dipy)_2]Cl_2,H_2O$. Crystal data are recorded. R. S. B.

Action of hot solutions of alkaline bases on mercuric iodide. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], **2**, 657—658).—Delwaulle's results (A., 1934, 265) are confirmed. D. R. D.

Behaviour of mercuriammonium compounds with potassium cyanide. S. AUGUSTI (Gazzetta, 1935, **65**, 117—119).—Mercuriammonium salts react with aq. KCN solutions liberating quantitatively 4 g.-mols. of KOH for every Hg_2N· radical, *e.g.*, $Hg_2NCl+8KCN+4H_2O \longrightarrow 2K_2[Hg(CN)_4]+4KOH+NH_4Cl$. Titration of the KOH permits a volumetric determination of Hg_2N·. O. J. W.

Preparation of permutite by the dry method. I, II. J. K. DELIMARSKI (J. Gen. Chem. Russ., 1934, **4**, 1400—1404, 1405—1406).—I. Permutite (I) prepared by Gans' method (cf. B., 1907, 872) disintegrates to a powder when treated with hot H_2O, rendering it unsuitable for technical purposes.

II [with F. G. SHAROVSKI]. The activity of (I) heated at 100—800° falls with rise in temp.; air-dried (I) is the most active. R. T.

Rare earths. II. [Scandium, yttrium, and lanthanum.] J. S. ŠTĚRBA-BÖHM and M. MELICHAR (Coll. Czech. Chem. Comm., 1935, **7**, 131—145; cf. this vol., 606).—The degree of hydrolysis of $0{\cdot}1N$ aq. acetates of Sc^{III}, Y^{III}, and La^{III} is 11·4%, 0·71%, and 0·31%, respectively. The complex *salt* $K_2[Sc(OH)_5H_2O],3H_2O$ (I) crystallises from solutions of $Sc(OAc)_3$ in conc. aq. KOH. Under similar conditions, $Y(OAc)_3$ affords crystals of $Y(OH)_3$. (I) decomposes in moist air. The following *substances* have been prepared: $(HCO_2)_3Sc$, $(HCO_2)_2ScOH$, $(HCO_2)_6Li_3Sc,3H_2O$, $(HCO_2)_6Na_3Sc$, $(HCO_2)_6K_3Sc$, $Sc(OH)(OAc)_2$, and $2Sc(OH)_3,H_2O$. J. G. A. G.

Indium salts of organic acids.—See this vol., 730.

Silicon oxyhalides. H. RHEINBOLDT and W. WISFELD (Annalen, 1935, **517**, 197—211).—$SiCl_4$ and O_2 (slight excess), when led through a porcelain tube at 1000°, give glassy, highly polymerised products; at 800° reaction is very slow; at 900° mainly Si_2OCl_6, m.p. −33°, b.p. 137°, is obtained; at 950—970° *octachlorotetrasiltetroxan* (I), $Si_4O_4Cl_8$, m.p. 77°, b.p. 92°/15 mm. (decomposed by H_2O), is also formed. $SiBr_4$ and O_2 do not react at 650°, and inflame at 705°, forming SiO_2 and Br; at 670—695° there are formed *hexabromodisiloxan*, Si_2OBr_6, m.p. 28·5°, b.p. about 120°/15 mm., and *octabromotetrasiltetroxan* (II), m.p. 123·5°, b.p. 170°/15 mm., both very sensitive to H_2O. (I) and (II) may be $X_3SiO{\cdot}SiX<^{O}_{O}>SiX{\cdot}OSiX_3$ or, more probably, $SiX_2<^{O{\cdot}SiX_2{\cdot}O}_{O{\cdot}SiX_2{\cdot}O}>SiX_2$. R. S. C.

Oxidation of graphite. III. V. SIHVONEN (Suomen Kem., 1935, **8**, **B**, 21—24; cf. A., 1934, 742).—A further discussion of the author's theory. F. L. U.

Structural changes taking place during the ageing of freshly-formed precipitates. III. Mechanism of ageing of lead sulphate precipitated at room temperature. IV. Ageing of fresh lead sulphate at room temperature in the air-dried state, and of precipitates covered with an adsorbed layer of wool-violet. I. M. KOLTHOFF and C. ROSENBLUM (J. Amer. Chem. Soc., 1935, **57**, 597—600, 607—611; cf. A., 1934, 1069).—III. Scarcely any ageing of $PbSO_4$ occurs in EtOH; in MeOH or 70% EtOH ageing is much slower than in H_2O. The retardation of ageing is due to the decreased velocity of recrystallisation, caused by the decreased solubility of $PbSO_4$.

IV. Air-dried $PbSO_4$ ppts. undergo scarcely any ageing when kept below R.H. 0·6, and do not absorb H_2O, but above R.H. 0·85 slow ageing occurs, which is ascribed to internal recrystallisation, whilst about 2% of H_2O is absorbed in the capillaries. When the ppt. is covered by an adsorbed layer of wool-violet the velocity of recrystallisation is greatly diminished and little ageing occurs. The external surface of fresh $PbSO_4$ can be determined by the radioactive method if the ppt. is covered with adsorbed wool-violet and then shaken with Th-*B* solution. E. S. H.

Reaction between nitrogen dioxide and water vapour. I. N. KUZIMINUIKH and V. S. UDINTZEVA (Khimstroi, 1934, **6**, 523—526).—The reaction between NO_2 and H_2O at 70—100° does not take place in the gaseous phase (cf. Burdik and Freed, A., 1921, ii, 313). This explanation is therefore not applicable to the oxidation of SO_2 by N oxides. CH. ABS. (*e*)

Fluorination of nitric acid. Nitroxyfluoride, NO_3F. O. RUFF and W. KWASNIK (Angew. Chem., 1935, **48**, 238—240; cf. this vol., 181).—NO_3F is formed quantitatively when F_2 is passed into 100% HNO_3 at room temp. in a quartz apparatus. Mol. wt., O, N, and F determinations give the theoretical vals. The v.p. is given by $\log p = -1044{\cdot}9/T + 7{\cdot}478$; m.p. −175°, b.p. −45·9°, heat of vaporisation 4726 g.-cal. per mol., Trouton's const. 20·8, $d_{liq.} = 2{\cdot}2148 - 0{\cdot}0031147$. Solid or liquid NO_3F is exploded by mechanical shock. It is stable in dry glass or quartz, but gives OF_2 and O_2 with H_2O, OF_2 with 2% NaOH, and O_2 with 20% NaOH, whence the formula $O_2N{\cdot}O{\cdot}F$ is proposed. Numerous chemical properties and the effect on the respiratory system are described. R. S.

Reaction of fluorine with nitric acid and with solid potassium nitrate to form NO_3F. D. M. YOST and A. BEERBOWER (J. Amer. Chem. Soc., 1935, **57**, 782).—The observations of Cady (this vol., 181) are confirmed and further reactions of NO_3F noted. E. S. H.

Products of hydrolysis of P_2I_4, and the preparation of hypophosphoric acid from it. J. H. KOLITOWSKA (Rocz. Chem., 1935, **15**, 29—36).—The products of hydrolysis of P_2I_4 by H_2O at 0° are H_3PO_2, H_3PO_3, H_3PO_4, PH_3, $P_{12}H_6$, and HI. $H_4P_2O_6$ (I) is obtained in 24% yield when P_2I_4 is added to aq. NaOH and H_2O_2, whilst when these are added to the above reaction mixture after 24 hr. of hydrolysis with H_2O ≯ 10% of (I) is produced. The method gives higher yields than other methods. R. T.

Preparation of inorganic reagents. I. Arsenic chloride. C. L. TSENG, M. HU, and M. HSÜ. **II. Phosphorus tribromide.** C. L. TSENG and T. S. HO. **III. Hydrobromic acid.** C. L. TSENG, T. S. HO, and P. T. CHIA. **IV. Mercuric bromide. V. Sulphuryl chloride.** C. L. TSENG and C. H. SZE (Sci. Quart. Nation. Univ. Peking, 1935, **5**, 317—323; 324—336, 337—341, 342—345, 346—349).—I. Dumas' method gave an optimum yield (85% of theory) when the reactants in the proportions As_2O_3 99 g., NaCl 261 g., and conc. H_2SO_4 213 c.c. were heated slowly (3—4 hr.) to 180°.

II. The yields of PBr_3 obtained by the different published methods were almost identical.

III. NaBr (103 g.), H_2O (80 c.c.), and conc. H_2SO_4 (35 c.c.) were mixed at 0° (approx.) and the distillate at < 200°, after repeated refractionation, afforded 85% of the stoicheiometric yield of const.-b.p. aq. HBr.

IV. An adaptation of the method of Baker and Watson, (J.C.S., 1914, **105**, 2531) is described.

V. The yield of SO_2Cl_2 synthesised by published methods from SO_2 and Cl_2 in the presence of camphor was 46% of stoicheiometric, based on the wt. of $NaHSO_3$ used. J. G. A. G.

Preparation of pure vanadium. A. MORETTE (Compt. rend., 1935, **200**, 1110—1112).—V has been prepared as a grey powder of 99·3% purity by the reduction of VCl_4 vapour by Mg at 700°, and of 98·9—99·5% purity by heating Mg with VCl_2 in an atm. of A or pure H_2 at ≯ 700° for 1—2·5 hr. The V powder burns in the Bunsen flame, reacts violently with conc. HNO_3 giving V_2O_5, and is dissolved by HF but not by HCl. M. S. B.

Manufacture of pure hydrofluoric acid.—See B., 1935, 451.

Preparation and properties of fluorine compounds. W. LANGE (Chem.-Ztg., 1935, **59**, 393—395).—A review.

Slow action of fuming nitric acid vapours on different elements. E. MONTIGNIE (Bull. Soc. chim., 1935, [v], **2**, 625—626).—Cl_2 is oxidised in the course of 1—2 months at room temp. (15—18°) to $HClO_3$, no $HClO_4$ being formed. Br is oxidised under the same conditions to $HBrO_3$, I to HIO_3, Se to SeO_2, and white P to H_3PO_4 and some H_3PO_3 (which is subsequently completely oxidised to H_3PO_4). As is oxidised superficially to As_2O_3, and Sb is oxidised to an even smaller extent. S and Te are not attacked. D. R. D.

Action of perchloric acid. J. R. PARTINGTON (Chem. and Ind., 1935, 468—469).—Mixtures of aq. $HClO_4$ and org. substances are liable to explode violently, even in the cold. J. G. A. G.

Reaction between iodine and oxalic acid in ethylene glycol as a solvent. B. K. CHATTERJEE and B. L. VAISHYA (J. Indian Chem. Soc., 1935, **12**, 137—138).—I and $H_2C_2O_4$ will not react in $(CH_2{\cdot}OH)_2$ (I), either in light or in the dark, even if as much as 50% by vol. of H_2O is mixed with it. If, as suggested by Griffith *et al.* (A., 1932, 1210), the intermediate formation of IOH takes place, the reaction ought to be favoured by (I). Earlier

work has shown the reaction to be ionic. It is evidently not independent of the medium, which should be such as to favour ionisation. M. S. B.

Preparation of trisodium periodate and periodic acid. J. LANGE and R. PARIS (J. Pharm. Chim., 1935, [viii], **21**, 403—405).—$Na_3H_2IO_6$ (yield 90—100%) is obtained by treating NaI (50 g.) in 10% NaOH (2000 g.) with Br (240 g.) at 80°. H_5IO_6 is prepared by treating Ag_2HIO_5 with Br. S. C.

Ter- and quadri-valent manganese [chlorides]. J. H. KŘEPELKA and J. KUBIS (Coll. Czech. Chem. Comm., 1935, **7**, 105—124).—A green solution containing $MnCl_4$ is obtained by passing dry HCl through an ethereal suspension of MnO_2 at −63°. At −76°, a brown solution containing more $MnCl_4$ is obtained. CCl_4 and light petroleum ppt. from these solutions a black unstable substance which affords in Et_2O a violet solution containing $MnCl_3$. By replacing MnO_2 with Mn_2O_3, $MnCl_3$ is obtained, but $MnCl_4$ could not be isolated. Earlier work is criticised. J. G. A. G.

Decomposition of permanganic acid and manganese dioxide. P. DUBOIS (Compt. rend., 1935, **200**, 1107—1110).—A conc. solution of $HMnO_4$, approx. 2·6*M*, crystallises at −11°. The crystals consist of ice containing varying quantities of $HMnO_4$. Exposure of the solutions to diffused daylight results in gradual elimination of O_3 and pptn. of impure MnO_2. This can be purified by repeated treatment with boiling HNO_3. Drying at 100° gives $MnO_2,0{\cdot}56H_2O$ (I). By treating $HMnO_4$ solution directly with boiling HNO_3 and drying the ppt. at room temp., pure $MnO_2,1{\cdot}66H_2O$ (II) is obtained. Both (I) and (II) begin to lose O_2 above 200° but retain some H_2O up to 500°. Before giving Mn_2O_3 at 600° they either undergo allotropic transformation or form an oxide approx. $MnO_{1.9}$. The anhyd. MnO_2, previously obtained by heating $Mn(NO_3)_2$ (A., 1934, 617), decomposes at 600° to Mn_2O_3. M. S. B.

Recent researches on certain of the rarer elements. G. T. MORGAN (J.C.S., 1935, 554—570).—A lecture. An exposition is given of the work published by the author and colleagues on the org. derivatives of Se and Te. The extraction of Ge and Ga from Northumberland coal ash is described: the ash is distilled with conc. HCl and $GeCl_4$ distils over whilst $GaCl_3$ remains in the still. Re has been isolated from Australian molybdenite. In the final separation, 2 : 2′-dipyridyl pptd. the Mo as dipyridyl molybdate, leaving the Re in solution. The following complex *salts* have been prepared: $K_2Na[ReO(CN)_4]$, $K_3[ReO(CN)_4]$, *2 : 2′ : 2″-tripyridyl rhenichloride*, *2 : 2′-dipyridyl rhenichloride*, *bis-2 : 2′-dipyridyl rhenichloride*, *2 : 2′ : 2″-tripyridyl perrhenate*, and *2 : 2′-dipyridyl perrhenate*. The following *co-ordination compounds* have been prepared (2 : 2′-dipyridyl= dipy), chiefly from $K_2[RuNOCl_5]$: *cis-* and *trans-*$[dipyRuNOCl_3]$, $[dipyRuNOBr_3]$, $[dipyRuNOI_3]$, $[(dipy)_2]^{\cdots}[RuNOCl_5]''$, $[dipy]^{\cdots}[RuOHCl_5]''$, [2 : 2′ : 2″-tripyridyl $RuNOCl_2]Cl,xH_2O$, and [tripyridyl $RuNOCl_2]_2[RuNOCl_5]$. J. G. A. G.

Reduction of ferric oxide by hydrogen and oxidation of metallic iron reduced from ferric oxide. Y. GOTOH (Ryojun Coll. Eng., Inouye Commem. Vol., 1934, 393—413).—Reduction of pure Fe_2O_3 to Fe by H_2 takes place in two stages, Fe_3O_4 being formed between 250° and 300°. As the temp. is raised the Fe produced goes into solid solution in the Fe_3O_4 until that contains 21%Fe, after which a vigorous reduction ensues and the whole is converted into Fe at 480°. On heating the reduced Fe in air the reverse process occurs, Fe_3O_4 being formed at 80—250° until the product contains 66%, after which no further reaction occurs below 360°; above this temp. magnetic Fe_2O_3 is formed which at > 500° is converted into the non-magnetic form and at > 850° into the rhombohedral form. FeO cannot be detected at any stage of either the oxidation or the reduction process. The effect of gas velocity on the rate of reduction and oxidation is shown graphically. A. R. P.

Change undergone by aqueous solutions of crystallised ferrous sulphate. R. SAN MARTÍN (Anal. Fís. Quím., 1935, **32**, 370—373).—Aq. $FeSO_4$ oxidises on exposure to air, basic $Fe^{\cdots}$ sulphate being pptd. and H_2SO_4 formed in solution. The reaction ceases when $[H_2SO_4]$ reaches a limiting val. and can be prevented by adding H_2SO_4. D. R. D.

Reactions in solid state at room temperature. A. SERRA (Period. Min., 1934, **5**, 175—179; Chem. Zentr., 1934, ii, 3913).—Various sulphide minerals (pyrites, Pb glance etc.) react with Ag, Zn, Sn, Au, Pb, or Cu foil or wire at room temp., giving a perceptible stain within 24 hr. J. S. A.

Basic salts. X. Chemistry and morphology of basic salts of bivalent metals. III. Basic cobalt chlorides. W. FEITKNECHT and G. FISCHER (Helv. Chim. Acta, 1935, **18**, 555—569; cf. this vol., 461).—By incomplete pptn. of aq. $CoCl_2$ with NaOH an unstable, green basic chloride (I), approx. $CoCl(OH),4Co(OH)_2,4H_2O$, is formed. The conditions affecting its stability have been studied, and its structure is discussed in the light of *X*-ray data. By ageing of (I) or by slow hydrolysis of aq. $CoCl_2$ a stable, rose-coloured basic chloride, $CoCl_2,3Co(OH)_2$, is formed. E. S. H.

Coloration of cobalt salts. C. DUVAL (Compt. rend., 1935, **200**, 934—936).—Electrophoresis in EtOH solution shows that the blue colour formed by $CoCl_2$ and LiCl is due to $Li[CoCl_3(H_2O)_3]$. The *compound* $H[CoCl_3(H_2O)_3]$ (I) is obtained by passing dry HCl over a mixture of equiv. parts of $CoCl_2$ and $CoCl_2,6H_2O$ at −5° in the dark and in contact with dry Et_2O. It is also obtained, together with $Co(OH)_2$ and HCl, by heating $CoCl_2,6H_2O$. It is decomposed by excess of H_2O. The hydrate $CoCl_2,2H_2O$ (II) is actually $Co[CoCl_3(H_2O)_3]_2$, and appears violet owing to the coexistence of a rose cation and blue anion. Passage of dry HCl through an Et_2O suspension of Co_2O_3 yields the green $Co[CoCl_6]$, which in air passes into (II). (I) yields blue salts with metals of which the polarisation potential is > that of Al. With other metals it forms complexes, *e.g.*, $[CdCl_6][Co(H_2O)_6][Cd(H_2O)_6]$. The rose hydrate is $[CoCl_6][Co(H_2O)_6]_2$. J. W. S.

Formation of basic sulphate and precipitation of nickel from solution by magnesium. G. GIRE

(Compt. rend., 1935, **200**, 1213—1215; cf. A., 1934, 159).—The amount of Ni deposited as $NiSO_4,4NiO,nH_2O$ from aq. $NiSO_4$ after dissolution of Mg therein increases with time towards a definite limit, which increases with dilution and with rise of temp. Higher temp. favours the attainment of equilibrium. This is due to a secondary reaction between SO_4'', $Ni^{\cdot\cdot}$, and OH' ions. The action of Mg also causes direct deposition of Ni, especially above 30°. Freshly pptd. $Ni(OH)_2$ does not react with $NiSO_4$.

J. W. S.

Mixed nickel nitrites of univalent and bivalent metals. I. A. Ferrari and C. Colla (Gazzetta, 1935, **65**, 168—176).—The prep. of the *compounds* $M_2Hg[Ni(NO_2)_6]$ is described (M=NH_4, K, and Tl). These are isomorphous with $K_2Pb[Ni(NO_2)_6]$ (I) and have *a* 10·46, 10·29, 10·42 Å., respectively. With Rb and Cs there is a tendency to form $2Rb_2Hg[Ni(NO_2)_6]Rb_2Hg[Hg(NO_2)_6]$ and $Cs_2Hg[Ni(NO_2)_6]Cs_2Hg[Hg(NO_2)_6]$, with *a* 10·50 and 11·04 Å., respectively. These are also isomorphous with (I), and probably consist of solid solutions between the two component complex nitrites. By increasing the Ni : Hg ratio to 2 : 1 in the prep. the compound $Rb_2Hg[Ni(NO_2)_6]$ can be obtained, but not the corresponding Cs compound. O. J. W.

Addition of hydrazine to nickel pyrophosphate. W. Daller (Oesterr. Chem.-Ztg., 1935, **38**, 76—77).—On adding aq. N_2H_4,H_2O (I) to a stirred solution of $NiCO_3$ in $H_4P_2O_7$, filtering, and drying, a greenish-blue compound (II) is obtained. Aq. (I), $H_4P_2O_7$, and $NiSO_4$ give a greenish-blue ppt. changing to a blue compound (III) on further addition of (I). On digesting with (I) (II) gives a reddish-violet compound (IV). A solution of $Ni_2P_2O_7$ in $Na_4P_2O_7$ gives with (I), after leaving in presence of EtOH for 6 weeks, a blue compound (V). The ppts. are dried by means of EtOH. The atoms of P and mols. of N_2H_4 per atom of Ni are (II) 1·132, 1·251, (II) 0·7005, 1·888, (IV) 0·5410, 3·000, and (V) 1·125, 1·817.

R. S. B.

Complexes formed between benzidine and metallic salts.—See this vol., 613.

Colorimetric determination of p_H at higher temperatures. III. W. Neumann (Z. anal. Chem., 1935, **101**, 89—101; cf. A., 1934, 500).—Na_2SO_4 shows a p_H displacement (I) on heating opposite in sign to that of KCl or NaCl. (I) is compounded of a change in the ionic product of H_2O, and of a change in the salt error (II) of the indicator. At 100°, (I) is practically the same for H_2O and for neutral salts, indicating that (II) tends towards zero. Comparative results are given for $CaCl_2$, $MgCl_2$, and $MgSO_4$.

J. S. A.

Indicator properties of some dinitro-derivatives. J. van den Haute (Natuurwetensch. Tijds., 1935, **17**, 64—71).—Absorption curves, λ for max. extinction coeff. (*E*), *K*, and the p_H at which a sharp colour change takes place (vals. given in parentheses) have been determined for 3 : 5- (λ 4200, *E* 73,500, *K* $0·91\times10^{-3}$, p_H 1·3—2·5) and 4 : 6-dinitroguaiacol (λ 4050, *E* 23,660, *K* $6·04\times10^{-7}$, p_H 5—7·5), 2 : 4-dinitrothymol (λ 4040, *E* 73,460, *K* $1·72\times10^{-4}$, p_H 2·2—3·4), and 4 : 6-dinitro-*o*-cresol (λ 4100, *E* 68,930, *K* $6·41\times10^{-5}$, p_H 2·4—3·8). These compounds are excellent indicators at concns. of 6×10^{-6} if a step photometer is used. S. C.

Determination of hydrogen with silver permanganate solution. F. Hein and W. Daniel (Z. anal. Chem., 1935, **99**, 385—390; cf. A., 1931, 1256).—The slow evolution of O_2 from the $AgMnO_4$ solution (I) sweeps out dissolved N_2, reabsorption of which may cause apparently high results for H_2 absorption. (I) should be resaturated with N_2 before use, and N_2 added to gases rich in H_2 to avoid error. J. S. A.

New methods of water analysis.—See B., 1935, 432.

Heavy water. W. Dominik (Polish Agr. Forestal Ann., 1934, **33**, 359—370).—Possibilities of using D_2O for the determination of OH and enolisable CO are discussed. Ch. Abs. (*e*)

Determination of chlorine in water by the *o*-tolidine method.—See B., 1935, 480.

Determination of small quantities of iodides. Application to the determination of small quantities of different metals. M. L. Jean (Bull. Soc. chim., 1935, [v], **2**, 605—616).—To determine < 0·01 g. of I′ in 20—30 c.c. of solution, the I′ is oxidised to IO_3' by aq. Br in presence of $NaHCO_3$, the excess of Br reduced by CH_2O in presence of NaOH at 0°, the solution acidified with AcOH, and the IO_3' determined iodometrically. CrO_4'' and Cr_2O_7'' are determined by adding a known quantity of I′ in acid solution, boiling off the I liberated, and determining the excess of I′ by the above procedure. $Cr^{\cdot\cdot\cdot}$ must first be oxidised to CrO_4'' (*e.g.*, by aq. Br, as in the oxidation of I′). Cr and I′ may also be oxidised to CrO_4'' and IO_3', respectively, using $KMnO_4$ in boiling alkaline solution and destroying the excess by means of EtOH, but the Br method is more convenient. $Ag^{\cdot}$ is determined by adding an excess of I′, adding aq. $Ba(NO_3)_2$ and Na_2CO_3 to carry down the ppt., filtering, and determining the I′ remaining in solution as already described. D. R. D.

Iodometric studies. III. Significance of concentration of iodide in dilute iodine solutions. R. V. Teis (J. Gen. Chem. Russ., 1934, **4**, 1364—1369).—The sensitivity of the starch–I reaction is greatest when the [KI] is ≮ 1%, for 0·001—0·002*N*-I.

R. T.

Detection of fluoride ions. L. Kulberg (J. Gen. Chem. Russ., 1934, **4**, 1440—1443).—The blue colour of aq. $Fe_4[Fe(CN)_6]_3$ is intensified by F′; this reaction serves for detection of ≮ $3·3\times10$ g. of F′, in presence of all other anions. R. T.

Measuring syringes and their application, especially to accurate determination of oxygen in water by Winkler's method. A. Krogh (Kem. Maanedsbl. nord. Handelsbl. kem. Ind., 1934, **15**, 105—109; Chem. Zentr., 1934, ii, 4002).—The micro-application of Winkler's $Mn(OH)_2$ method is described, using graduated hypodermic syringes for titration.

J. S. A.

Potentiometric determination of sulphite. G. Spacu and C. Drăgulescu (Z. anal. Chem., 1935, **101**, 113—116).—SO_3'' is titrated potentiometrically with $HgCl_2$ in aq. EtOH solution, the end-point

corresponding with formation of $Na_2[Hg(SO_3)_2]$. O_2 and light should be excluded. J. S. A.

[Detection of sulphurous acid and its salts and of tin.] H. Freytag (Ber., 1935, 68, [*B*], 585—586; cf. A., 1934, 1321).—A reply to Feigl *et al.* (this vol., 462). H. W.

Application of acetone solutions of sulphur dioxide to the gravimetric determination of selenium. V. Hovorka (Chem. Listy, 1935, **19**, 73—75).—H_2SeO_3 is rapidly and quantitatively reduced to Se by $COMe_2$ saturated with SO_2; the presence of HCl is indispensable, pointing to the probability that Se_2Cl_2 is an intermediate product. R. T.

Conductometric determination of selenocyanides in presence of cyanides. R. Ripan-Tilici (Z. anal. Chem., 1935, **100**, 405—408).—Two breaks are obtained in the conductivity–titration curve, corresponding with formation of $[Ag(CN)_2]'$ and with complete pptn. of AgCN+AgCNSe, whence CNSe′ may be calc. J. S. A.

Potentiometric determination of selenocyanide in presence of halides. P. Spacu (Z. anal. Chem., 1935, **100**, 397—405).—SeCN′ may be titrated potentiometrically in presence of I′+Cl′ or Br′+Cl′, but the SeCN′ and Br′ end-points cannot be separated in presence of I′. J. S. A.

Detection of tellurium. M. Ishibashi and S. Mori (J. Chem. Soc. Japan, 1934, **55**, 1262—1272).—The mineral powder is dissolved in hot H_2SO_4, diluted, and Cu is added. Red $TeSO_3$ is formed. Ch. Abs. (*e*)

Determination of small quantities of tellurium in lead.—See B., 1935, 459.

Absorption of ammonia in boric acid. F. J. Watson (J. Soc. Chem. Ind. Victoria, 1933, **33**, 799—801).—NH_3 may be distilled into H_3BO_3 and titrated directly with HCl, absorption being complete when a large excess of cooled aq. H_3BO_3 is used. J. S. A.

Hydroxyapatite precipitation as basis for volumetric determination of phosphoric acid in solutions containing calcium. P. Damsgaard-Sørensen (Kem. Maanesdbl. nord. Handelsbl. kem. Ind., 1934, **15**, 73—79; Chem. Zentr., 1934, ii, 3992).—H_3PO_4 may be titrated with NaOH, using Me-red+phenolphthalein as indicator, and matching the primary (I) and secondary end-points against citrate–HCl and borate–HCl buffers, respectively. In presence of excess of Ca, titration with NaOH [or titration with aq. $Ca(OH)_2$ if Ca is absent] to a permanent red colour ppts. hydroxyapatite, $3Ca_3(PO_4)_2,Ca(OH)_2$, and requires exactly 3·5 times the NaOH to reach (I). PO_4''' in 0·01*N* solution may be so titrated. J. S. A.

Elimination of phosphate ion in systematic qualitative analysis. E. Kahane (Ann. Chim. Analyt., 1935, [iii], **17**, 119—121).—NH_4OAc and then an excess of $FeCl_3$ are added to the solution, which is made just alkaline with aq. NH_3. On boiling the solution until free NH_3 is completely removed, PO_4''' is pptd. with the Fe, Al, and Cr without carrying down traces of Zn, Ba, Sr, Co, or Mn as in the usual procedure. J. S. A.

Determination of small amounts of arsenic. J. Gangl (Oesterr. Chem.-Ztg., 1935, **38**, 64—69).—As is rapidly and completely reduced to AsH_3 by Zn dust and H_2SO_4 in a modified Marsh apparatus. The As is quantitatively deposited as a mirror (I) by passing the gas through a narrow SiO_2 tube heated to 500°, the AsH_3 being completely expelled from solution by boiling in a stream of H_2. Quantities of As $<10^{-6}$ g. may be determined by matching (I) against a standard. With larger amounts ($1-100\times 10^{-6}$ g.) (I) is dissolved in ICl, and the liberated I titrated in acid solution with KIO_3 in presence of KCN, using a drop of CCl_4 as indicator. Reduction to As with NaH_2PO_2 is applicable for very small quantities only in the absence of other reducible metals. J. S. A.

Determination of small quantities of arsenic. C. J. Snijders, jun., and A. J. W. van der Drift (Chem. Weekblad, 1935, **32**, 275—280).—200 c.c. of the neutral solution containing $\ddagger$ 0·01 mg. of As are refluxed for 30 min. with 2—3 g. of $FeSO_4,7H_2O$, 10—15 drops of 40% $SnCl_2,2H_2O$ in conc. HCl, 50 c.c. of 1 : 1 HCl, and 12—15 g. of Zn previously activated by immersion in acidified $SnCl_2$ solution. The gas evolved (H_2 and AsH_3) is washed with 15% CuCl in 1 : 1 HCl, and passed through a filter-paper soaked in $HgBr_2$ solution. The stain is developed by immersion for 2 min. in 20% aq. CdI_2, dried, and compared with a standard. An accuracy of 0·001 mg. may be obtained. D. R. D.

New indicators for bromometric titrations. T. Sotgia-Rovelli (Boll. Chim. farm., 1935, **74**, 265—270, 273—276).—If in the reaction $3H_3AsO_3+KBrO_3=3H_3AsO_4+KBr$, Me-orange (I) is used as indicator, it is decolorised by Br liberated by excess of $HBrO_3$; (I), however, reacts slowly. More suitable are Ponceau-3R, methylene-blue, or Bordeaux-B (all for titration of 0·1 or 0·01*N* solutions), or safranine, Azure-II, chrysoidine, or saffron-yellow (for 0·1*N* solutions). Fuchsin and litmus are unsuitable. E. W. W.

Electrical conductivity method for determining carbon dioxide and other reactive gases. R. G. Newton (Ann. Bot., 1935, **49**, 381—398).—Apparatus for micro-determinations is described. A. G. P.

Determination of small concentrations. VIII. Carbon monoxide. A. V. Pamfilov and S. L. Kagan (J. Gen. Chem. Russ., 1934, **4**, 1390—1393).—The usual methods are untrustworthy when the [CO] is $<$ 1 mg. per litre. R. T.

Conductometric determination of cyanates in presence of cyanides. R. Ripan-Tilici (Z. anal. Chem., 1935, **99**, 415—418).—CNO′ may be titrated conductometrically with $AgNO_3$ in presence of CN′. Breaks in the curve correspond with formation of $[Ag(CN)_2]'$ and with complete pptn. of AgCN+AgCNO. J. S. A.

Silicic acid and silicates. IV. Determination of silicic acid in insoluble silicates. F. W.

MEIER and L. STUCKERT (Z. anal. Chem., 1935, **101**, 81—84; cf., B, 1932, 549).—The silicate is fused with $CaCO_3+NH_4Cl$ to avoid subsequent formation of $KClO_4$. The melt is extracted with H_2O, and the insol. residue heated with $HClO_4$. The insolubilised SiO_2 is then washed with 10% HCl and ignited. J. S. A.

Quantitative spectrographic analysis of alkali metals. Application to cæsium in mineral waters. R. BOSSUET (Compt. rend., 1935, **200**, 1094—1096).—0·025 c.c. of conc. mineral H_2O, or of a solution of the alkali chlorides previously separated, is volatilised in the O_2–C_2H_2 flame and the emission spectrum photographed. By increasing the dilution the limit at which the ultimate ray of Cs, λ 4555·3 Å., disappears may be determined. The [CsCl] of a no. of mineral waters is given. The same method may be applied to the determination of traces of Rb. M. S. B.

Quantitative spectral analysis. III. R. BRECKPOT and A. MEVIS (Ann. Soc. Sci. Bruxelles, 1935, **55**, B, 16—30; cf. A., 1934, 857).—Data are given for the spectral determination of Li, Na, K, Sr, Bo, Si, P, Te, and Tl using a CuO base. R. S.

Argentometric determination of sodium hydroxide and sodium sulphide in sodium aluminate.—See B., 1935, 451.

Determination of sodium [in water] by means of zinc uranyl acetate.—See B., 1935, 432.

Determination of small quantities of silver in water. J. JUST and A. SZNIOLIS (Arch. Chem. Farm., 1935, **2**, 170—175).—Two drops of 10% aq. KI and 5—10 drops of 50% HCl are added to 100 ml. of H_2O, the solution is filtered through a membrane (I) of porosity 1 μ and of diameter 2·5 cm., 2 ml. of aq. H_2S are then passed through the (I), and the density of coloration of the (I) is compared with that given by standard solutions containing 0, 0·05, 0·1, 0·15, and 0·2 p.p.m. of Ag. The method can be applied to determine 0·0025 p.p.m. of Ag by increasing the vol. of the sample, and diminishing the diameter of the (I). R. T.

New indicators for argentometric titrations. E. CHIRNOAGĂ (Z. anal. Chem., 1935, **101**, 31—38).—Diphenylcarbazone may be used as an adsorption indicator in neutral solution, starch being added to stabilise the Ag halides in the colloidal state. $Fe_3[Fe(CN)_6]_2$ containing an excess of $Fe(CN)_6'''$ may also be used in presence of NaOAc, turning white or yellow at the end-point. J. S. A.

Determination of small amounts of silver with dithizone. H. FISCHER, G. LEOPOLDI, and H. VON USLAR (Z. anal. Chem., 1935, **101**, 1—23).—The Ag solution, containing about 12×10^{-6} g. of Ag per c.c., is acidified with HNO_3 and treated with successive measured small amounts of a standard solution (I) of dithizone (II) in CCl_4 [2—4 mg. of (II) per c.c.], until the green colour of (I) persists. Ag is determined from the vol. of (I) required, or colorimetrically in the united extracts. Pb, Zn, Cd, As, Sb, Bi, and Au do not interfere, Ag being extracted preferentially. In presence of Hg or > 10% of Cu, Ag+Hg or Cu is extracted with (II), and Ag extracted with KCNS. The KCNS solution is evaporated with H_2SO_4, the residue dissolved in 15% HNO_3, and Ag titrated. $0·1—2\times10^{-6}$ g. of Ag may be determined colorimetrically by shaking with the violet solution of the Cu–(II) compound, and matching the mixed colour against a standard Ag solution. J. S. A.

Detection of calcium, strontium, and barium in their mixtures. N. A. TANANAEV (Z. anal. Chem., 1935, **100**, 391—394).—On extraction of the dry nitrates with glacial AcOH, Ca and Mg dissolve, and may be quantitatively separated from Ba and Sr. Traces of Ca in presence of much Sr and Ba, but in absence of Mg, give an opalescence on evaporating with saturated aq. $K_4Fe(CN)_6$ and redissolution in H_2O. J. S. A.

Argentometric determination of barium oxide and barium sulphide in barium aluminate.—See B., 1935, 451.

8-Hydroxyquinoline and its application to [the determination of] magnesium. D. C. VUCETICH (Rev. fac. cienc. quim., La Plata, 1934, **9**, 81—91).—The complex salt is pptd. in presence of NH_3, NH_4Cl, and $COMe_2$, washed, redissolved in HCl, and determined with $KBrO_3$. Advantages over other methods are claimed. F. A. A.

Colorimetric determination of zinc with dithizone. W. DECKERT (Z. anal. Chem., 1935, **100**, 385—390).—To 50 c.c. of H_2O+1 c.c. of a saturated solution of dithizone (I) in 0·01*N*-NaOH, a measured vol. of the Zn solution is added until $1—3\times10^{-6}$ g. of Zn (matched roughly against standards) is present. The solution is diluted to 100 c.c. and examined colorimetrically. Alkalinity and excess of (I) must be identical for sample and standard. Urine and fæces are first oxidised with $H_2SO_4+HNO_3$, or ashed dry below 450°. Cu is removed by adding 2 drops of aq. $CuSO_4$ and pptg. with H_2S. The filtrate is exactly neutralised, and Zn determined as above. J. S. A.

Reaction of aminobenzoic acids with cadmium and zinc salts. J. V. DUBSKÝ and J. TRTÍLEK (Chem. Listy, 1935, **19**, 76—77).—Aq. *p*-$NH_2\cdot C_6H_4\cdot CO_2K$ and Cd salts yield a cryst. ppt., $(p\text{-}NH_2\cdot C_6H_4\cdot CO_2)_2Cd,2H_2O$ (I); Zn salts are not pptd. under analogous conditions. Cd cannot be quantitatively separated from Zn by pptn. as (I), which is extremely sol. in dil. acids and fairly sol. in H_2O. The solubility of $(m\text{-}NH_2\cdot C_6H_4\cdot CO_2)_2Cd$ is > that of (I). R. T.

Quantitative separation of metals by hydrogen sulphide. VII. Separation of zinc from chromium and a new method of separating chromium from nickel, cobalt, and iron. H. KATÔ (J. Chem. Soc. Japan, 1934, **55**, 1152—1155).—At p_H 2·3—4·0 Zn is pptd. as ZnS by H_2S while Cr remains in solution. At p_H 5 (with AcOH and NaOAc buffer) Ni, Co, and Fe are pptd. as sulphides from a solution containing Ni, Co, Fe, and Cr. Cr remains in solution. CH. ABS. (*e*)

Induced precipitation in analysis. I. H. KATÔ (J. Chem. Soc. Japan, 1934, **55**, 1148—1151).—The induced pptn. of $Zn(OH)_2$ by the presence of $KMnO_4$

is probably of chemical nature, but that of FeS by ZnS is due to adsorption. CH. ABS. (e)

Importance of p_H for determination and separation of metals by anthranilic acid. H. GOTÔ (J. Chem. Soc. Japan, 1934, 55, 1156—1163).—The min. p_H for complete pptn. and the max. p_H at which no pptn. takes place by anthranilic acid were respectively for Zn 4·72, 3·76; Cd 5·23, 4·25; Ni 4·51, 3·64; Co 4·41, 3·36; Mn 5·15, 4·10; Cu 2·79, 1·40. Cu can be pptd. alone from a solution containing the above metals. CH. ABS. (e)

Electrolytic determination of very small amounts of lead. A. NECKE and H. MÜLLER (Angew. Chem., 1935, 48, 259—261; cf. A., 1929, 286).—Pb is anodically deposited as PbO_2 from HNO_3 solution. The deposited Pb is determined colorimetrically by treating the PbO_2 with a 1% solution of " tetramethyl base " in AcOH. The method is applicable to 0·02—0·1 mg. of Pb in presence of a large excess of Cu. J. S. A.

Examination by a radioactive method of the quantitative analysis of very small amounts of lead by the method of P. Schmidt and co-workers. W. MESSERSCHMIDT and G. TARTLER (Angew. Chem., 1935, 48, 261—263).—Th-*B* was added to solutions of $Pb(NO_3)_2$ and the Pb deposited anodically as PbO_2 (cf. preceding abstract). Comparison of the Th-*B* in the deposit with that originally added to the solution, as measured by the γ-ray activity of the equilibrium products, showed that anodic deposition of $>$ 0·03 mg. of Pb was practically quant. Some Th-*C* (*i.e.*, Bi), but no Th-*B* (Pb), was deposited on the cathode. J. S. A.

Reactions of potassium iodide and bases with salts of lead, bismuth, mercury, copper, cadmium, and antimony. I. M. KORENMAN (Z. anal. Chem., 1935, 99, 402—410).—Aq. KI+a variety of aromatic and cylic bases give insol. products with Pb, Bi, Hg, Cu, Cd, and Hg salts which are in no case strictly sp. Sensitive tests are given by C_5H_5N for Pb, by 8-hydroxyquinoline for Bi, and by *p*-aminodimethylaniline for Cu. J. S. A.

Determination of metals with anthranilic acid. IV. Determination of lead and mercury. H. FUNK and F. RÖMER (Z. anal. Chem., 1935, 101, 85—88; cf. A., 1934, 621).—Hg and Pb are pptd. as Hg[or Pb]$(C_7H_6O_2N)_2$ by addition of anthranilic acid to the cold neutral solution. The ppts. may be dried at 105°; the Pb, but not the Hg, compound may be titrated with $KBrO_3$. Pptn. of Hg is not quant. in presence of alkali chlorides. J. S. A.

Determination of lead in drinking water.—See B., 1935, 432.

***p*-Homosalicylaldoxime as a reagent for copper.** C. H. KAO and K. H. CHEN (J. Chinese Chem. Soc., 1935, 3, 22—26).—*p*-OH·C_6H_3·CH:NOH is recommended for detection and determination of Cu in solution acidified with AcOH and of Ni in neutral or slightly alkaline solution. Details are given for the separation of these metals from other metals and from each other. J. W. S.

Potentiometric determinations in alkaline solution. Determination of copper and silver. C. DEL FRESNO and E. MAIRLOT (Anal. Fís. Quím., 1934, 32, 280—285).—In the potentiometric titration of alkaline solutions containing Ag and Cu with $VOSO_4$, the successive breaks correspond with the completion of the reactions $Ag^{\cdot} \longrightarrow Ag$, $Cu^{\cdot\cdot} \longrightarrow Cu^{\cdot}$, and $Cu^{\cdot} \longrightarrow Cu$. An accuracy of 1% may be obtained in the determination. D. R. D.

Analysis by means of organic compounds. I. Separation and determination of copper and cadmium by salicylaldoxime and electrolysis. II. Separation and determination of copper and cadmium by salicylaldoxime and hydroxyquinoline. III. Separation and determination of copper and lead by salicylaldoxime. M. ISHIBASHI and H. KISHI (J. Chem. Soc. Japan, 1934, 55, 1060—1064, 1065—1066, 1067—1069).—I. Cu can be pptd. by salicylaldoxime (I) from a slightly acid solution containing Cu and Cd. Cd is determined by electrolysis of the filtrate, (I) favouring the deposition of Cd.

II. Cu is pptd. as above, Cd being pptd. from the filtrate as $Cd(C_9H_6ON)_2$, which is dried at 130° and weighed.

III. Cu is pptd. from the slightly acid solution, as above, by (I). NH_3 is added to the filtrate until the p_H is $>$ 6·5, Pb being then pptd. by (I), collected, and dried at 105°. CH. ABS. (e)

Systematic potentiometric analysis. III. Separation and determination of mercury. W. HILTNER and W. GITTEL (Z. anal. Chem., 1935, 101, 28—31; cf. this vol., 185).—Hg, As, Sb, and Sn are separated as thio-salts by treatment with Na_2S. HgS alone is pptd. by addition of H_2O_2, and is titrated potentiometrically with KI after dissolution in HCl–HNO_3. J. S. A.

Ammonium molybdate as a microchemical reagent. C. VAN ZIJP (Pharm. Weekblad, 1935, 72, 414—418).—Characteristic cryst. compounds are obtained when NH_4 molybdate (I) is added to solutions containing Al, $Mn^{\cdot\cdot}$, or $Ce^{\cdot\cdot}$; less characteristic ppts. are obtained with Zn, Ni, Co, Cr, $Fe^{\cdot\cdot\cdot}$, Cu, Hg, Tl, or Ag and no result is produced with UO_2, Pb, Cd, Bi, Li, Mg, Ca, Sr, Ba, and $Fe^{\cdot\cdot}$. (I) can sometimes be replaced by the K, Cs, or Rb but not by the Na salt. S. C.

Analysis of felspar.—See B., 1935, 451.

Determination of metallic iron in presence of iron oxides. Reduced iron. F. HARTLEY, W. H. LINNELL, F. E. READ, and H. G. ROLFE (Quart. J. Pharm., 1935, 8, 100—112).—The B.P. (1932) method gives inaccurate and variable results. A modification of the method of Wilner (Merck, Z. anal. Chem., 1902, 41, 710) is satisfactory. F. O. H.

Determination of iron in presence of titanium; an aëration process. W. M. THORNTON, jun., and R. ROSEMAN (J. Amer. Chem. Soc., 1935, 57, 619—621).—The procedure of Gooch and Newton (A., 1907, ii, 507) has been modified by using air instead of Bi_2O_3 as the differential oxidising agent. E. S. H.

Ammonium salt of nitrosophenylhydroxylamine as a quantitative reagent. E. BENEDETTI (Rev. fac. cienc. quim., La Plata, 1934, 9, 59—68).—

The conditions under which this compound may be used to determine Fe^{III}, Fe^{II}, and Cu^{II} are described. F. A. A.

Determination of cobalt by means of nitroso-β-naphthol. L. Philippot (Bull. Soc. chim. Belg., 1935, **44**, 140—153).—Co nitroso-β-naphthol obtained from 50 c.c. of *M*-$CoSO_4$ is dried and decomposed by fuming HNO_3 (10 c.c.). Br (one drop) and conc. H_2SO_4 (20 c.c.) are added to the solution, which is then evaporated to fuming. H_2O (30 c.c.) is added, the solution boiled, neutralised by aq. NH_3 (50—60 c.c.) after addition of a further 30 c.c. of H_2O, and electrolysed for 24 hr. The determination of Co in presence of Ni, Zn, and Fe is described. The time can be reduced if after addition of conc. H_2SO_4 the solution is diluted, neutralised with K_2CO_3, and boiled. Br (3—4 drops) and 2*N*-KOH (20 c.c.) are added and the ppt. is dissolved in $H_2SO_4+H_2O_2$. The solution is made alkaline with NH_3 and electrolysed for 3·5 hr. The method gives good results when applied to the analysis of mineral sulphides. R. S.

$Hg(SCN)_4$" as reagent for cobalt. Comparison of $Na_2Hg(SCN)_4$, $K_2Hg(SCN)_4$, and $(NH_4)_2Hg(SCN)_4$. B. V. J. Cuvelier (Z. anal. Chem., 1935, **101**, 108—113).—$Na_2[Hg(SCN)_4]$ is the most sensitive reagent, $Co[Hg(SCN)_4]$ being less sol. in NaCl than in KCl or NH_4Cl solutions. J. S. A.

Organic [external] indicator for dichromate titrations. P. F. Thompson and E. C. Alabaster (J. Soc. Chem. Ind. Victoria, 1933, **33**, 810—811).—Diphenylcarbazide in presence of AcOH gives a pink colour with excess of CrO_4". In presence of Cu or Sn, HCl is added. J. S. A.

Reactions in the iodometric determination of chromates. F. L. Hahn (J. Amer. Chem. Soc., 1935, 57, 614—616).—The excess of $Na_2S_2O_3$ consumed in the reaction is ascribed to the formation of a complex chromic thiosulphate, which reacts slowly with I. E. S. H.

Separation of molybdenum in alloy steels, especially from tungsten, and its potentiometric determination.—See B., 1935, 458.

Determination of titanium in ferrous alloys.—See B., 1935, 410.

Determination of zirconium with 8-hydroxyquinoline. G. Balanescu (Z. anal. Chem., 1935, 101, 101—108).—In presence of ≤ 5 c.c. of HNO_3 per 10 mg. of Zr, 8-hydroxyquinoline ppts. Zr as $Zr(C_6H_6ON)_4$. The ppt. may be dried at 140° and weighed directly, titrated with $KBrO_3$, or ignited to ZrO_2. Ppts. of indefinite composition are obtained in presence of Cl'. J. S. A.

Detection of bismuth with sulphur-containing organic reagents. IV. J. V. Dubský, A. Okáč, and J. Trtílek (Z. anal. Chem., 1935, **100**, 408—419).—Compounds containing thio- and thiol-S in 1 : 3-positions (*e.g.*, 3-thiol-5-thio-1 : 2 : 4-triazole and -4-phenyltriazole, persulphocyanic acid, and trithioallophanic acid) give sensitive orange to brilliant red insol. Bi compounds of general type BiB_3, BiB_2Cl, and $BiBCl_2$. Compounds with similarly linked (thiol and thioether) S atoms in 1 : 3-positions give non-sp. yellow colorations. Cu", Ag, Pb, and Hg" tend to give non-sp. ppts. with both classes of compounds. J. S. A.

Volumetric determination of niobium. J. A. Tschernichov and M. P. Karssajevskaja (Z. anal. Chem., 1935, **99**, 398—402).—Contrary to the findings of Schwarz (A., 1934, 632), Nb cannot be determined accurately by reduction with Zn amalgam and re-oxidation with standard $FeCl_3$. J. S. A.

Action of sulphuric acid on platinum–gold–silver alloys and its importance in docimacy. K. W. Fröhlich (Z. Elektrochem., 1935, **41**, 207—211).—The usual method for determining Pt and Au is subject to errors due to dissolution of Pt and, to a smaller extent, of Au by H_2SO_4. The potential–temp. curves of Pt and Au intersect at 270°, above which the former is less "noble." Introduction of 1% of As_2O_3 into the H_2SO_4 used reduces the loss of Au to 1/5—1/6, and of Pt to 1/10—1/20, of that occurring with the pure acid, whilst the dissolution of Ag remains unaffected. F. L. U.

Thermoregulator, operating without a relay. M. Centnerszwer and J. Szper (Rocz. Chem., 1935, **15**, 26—28).—A PhMe thermoregulator is described. R. T.

Photo-electric temperature regulator. B. Lange and E. Voos (Z. techn. Physik, 1934, **15**, 323—326; Chem. Zentr., 1934, ii, 3794).—The regulator is operated by a mirror galvanometer, a Se cell, and a thyratron. A constancy of ±0·17° up to 1000° is claimed. H. J. E.

Standard tables for chromel–alumel thermocouples. W. F. Roeser, A. I. Dahl, and G. J. Gowens (J. Res. Nat. Bur. Stand., 1935, **14**, 239—246).—The tables give the thermal e.m.f. of chromel *P*–alumel, chromel *P*–Pt, and alumel–Pt over the range −310° to 2500° F. E. S. H.

Methods of testing thermocouples and thermocouple materials. W. F. Roeser and H. T. Wensel (J. Res. Nat. Bur. Stand., 1935, **14**, 247—282).—The methods developed and used at the National Bureau of Standards are described. E. S. H.

Experiments at very low temperatures obtained by the magnetic method. I. Production of low temperatures. N. Kürti and F. Simon (Proc. Roy. Soc., 1935, **A**, **149**, 152—176).—The production of very low temp. by the magnetic method is discussed with reference to the influence of the initial conditions of field and temp. and the characteristic properties of the substance. With the apparatus used it is possible, with even small amounts of substance, to maintain the low temp. for a very long time so that measurements may be carried out. $FeNH_4(SO_4),12H_2O$, $MnSO_4,(NH_4)_2SO_4,6H_2O$, $KBr(SO_4)_2,12H_2O$, and $Gd_2(SO_4)_3,8H_2O$ have been investigated as working substances. The first of these is the most satisfactory, and starting at 1·2° abs. and 14 kilogauss a temp. of 0·038° abs. is reached. L. L. B.

Apparatus for m.-p. determinations and pressure, vapour pressure, and thermo-regulators. P. C. Henriquez (Chem. Weekblad, 1935, **32**, 239—242).—For determining m.p., a closed tube is

fitted with a silvered vac. jacket containing windows for observing the substance in a capillary tube attached to the thermometer. The stirred liquid is heated electrically by an immersion element. A pressure regulator is operated electrically, and another by the inability of Hg to pass through a sintered glass plate; the amount of air passing through the apparatus is regulated by suction through a porous porcelain tube. A compact v.-p. regulator using very small quantities of liquid is described. A temp. accurate to 0·01° can be obtained with a Hg regulator having a bulb the size of a Beckmann thermometer, a capillary tube 0·05 mm. diameter, and a Pt contact 0·025 mm. thick. S. C.

Instruments for measuring spectral absorption. W. J. H. Moll, H. C. Burger, and W. J. Reichert (J. Sci. Instr., 1935, **12**, 148—152).—The normal spectrograph slit is replaced by a device containing seven slits, two of which have identical widths and the remainder known fractional widths. Identical light beams are passed through cells containing solution and solvent and then through the special slits. The absorption coeffs. are found by a graphical method from the seven spectra, which are compared by means of a microphotometer. C. W. G.

Illumination of the spectrograph in quantitative spectral analysis. R. Breckpot and L. Lialine (Ann. Soc. Sci. Bruxelles, 1935, **55**, B, 30—42).—The influence on the image of different types of illumination and size of slit is discussed. The best results are obtained with a lens of focal length 16·8 cm. between the source and the collimator, and slits of 0·01—0·025 mm. R. S.

Infra-red photography of coal. J. J. Walker and L. Slater (Nature, 1935, **135**, 623).—Advantages are discussed. L. S. T.

Sensitivity of photon counters. R. Audubert (Compt. rend., 1935, **200**, 918—920).—The sensitivity of photon counters, measured by comparison with a Hg-vapour resonance lamp, can reach 5×10^{-11} erg per sec. per sq. cm. with an Al cathode or $1{\cdot}0\times10^{-9}$ erg per sec. per sq. cm. with a CuI cathode. In either case there is a wide variation between the sensitivities of individual cathodes. The sensitivity increases rapidly with increasing voltage, but is independent of the residual gas in the cell. The best results are obtained with a plate or disc cathode and a wire or ring anode. The emission from various reactions studied varies from 10^{-6} to 10^{-9} erg per sec. per sq. cm. J. W. S.

Christiansen light filter. E. D. McAlister (Smithsonian Misc. Coll., 1935, **93**, 1—12).—Construction, advantages, and limitations are described. N. M. B.

Allison magneto-optic (A) method of analysis. M. A. Jeppesen and R. M. Bell. **(B) Apparatus.** T. R. Ball (Physical Rev., 1935, [ii], **47**, 546—548, 548—551).—(A) Readings taken by a no. of investigators indicate that the Allison minima are not a function of the chemical solutions used.

(B) A comprehensive statistical study, using the Allison apparatus, is described. Results are inconclusive. N. M. B.

Circular dichroism and some physico-chemical applications. J. P. Mathieu (Ann. Physique, 1935, [xi], **3**, 371—460).—A visual method of measurement in the visible range, and a modified form of Brace's method (cf. Physical Rev., 1904, **18**, 70) for the ultra-violet, are described. $Cr(OH)_3$ in tartaric acid first forms a Cr tartrate which passes spontaneously into a complex chromotartrate as shown by the absorption spectrum and by optical activity. Investigation of the circular dichroism appearing shows that the formation is a second-order reaction. In alkaline solution the complex acts as a weak acid. Neutralisation by an alkali shows a regular variation of ionic and optical properties and indicates the formation of an alkaline chromotartrate giving in presence of alkaline tartrate an alkaline chromotritartrate marked by optical activity; the structure and equilibrium of this compound are investigated. Analogous compounds are formed by Fe, Co, and Al. N. M. B.

Linear photo-electric densitometer. C. W. Miller (Rev. Sci. Instr., 1935, [ii], **6**, 125—127).—A portable instrument using a.c. and giving readings very nearly $\propto$ density is described. It can be adapted to measuring the blackness of opaque objects. N. M. B.

Photo-electric conductive substances. IV. Filters for the thallium cell. C. Asai (J. Chem. Soc. Japan, 1934, **55**, 1099—1101).—A glass plate painted with a 0·5% tartrazine solution absorbs $\lambda\lambda<4900$ Å., and is a suitable filter. Ch. Abs. (e)

Apparatus for photo-electric extinction measurements. S. Bodforss (Svensk Kem. Tidskr., 1935, **47**, 41—50).—The method uses a Hg lamp, optical filters, and two Se "sperrschicht" cells. Examples are given of its use in studying rapid reactions, phenolphthalein+NaOH, reduction of $PhN_2{\cdot}C_{10}H_6{\cdot}NH_2$-α, Me-orange, and methylene-blue by $SnCl_2$, and reduction of $HAuCl_4$ by H_2O_2. R. P. B.

Cæsium photo-elements sensitised by sulphur. V. Roshdestvenski (J. Tech. Phys. U.S.S.R., 1934, **4**, 669—670).—The Ag cathode is treated with S vapour instead of with O_2. The cell is not sensitive in the infra-red and has one max. in the visible. Ch. Abs. (e)

Photo-electric conductive substances. III. Spectroscopic studies on the photo-electric conductive thallium cell. C. Asai (J. Chem. Soc. Japan, 1934, **55**, 979—990).—The Tl cell is photosensitive from 5100 to 12,000 Å. (max. at 6480, 9550 Å.). Ch. Abs. (e)

Circuit for the analysis of Geiger-counter pulses. W. E. Ramsey and M. R. Lipman (Rev. Sci. Instr., 1935, [ii], **6**, 121—125).—A circuit for measuring the variation of the counting rate with the votage on the counter, the sizes of the pulses, the time of recovery, and the form of the recovery curve is described. N. M. B.

Apparatus for unipolar micro-electrolysis. S. Wehrli (Helv. Chim. Acta, 1935, **18**, 546—548).—An apparatus for the micro-determination of Pb by anodic deposition as PbO_2 is described. The anode

is a Pt wire; the Pb solution is separated from the cathode by a " diaphragm " of NH_4NO_3 solution. E. S. H.

Electron microscope using purely magnetic fields. R. Wallauschek and P. Bergmann (Z. Physik, 1935, **94**, 329—347).—The general theory of the microscope is given, and is applied to determine the optical consts. of instruments with magnetic lenses. A. B. D. C.

Securing rigidity of electrodes in conductometric work. B. N. Sastri and M. Sreenivasaya (J. Sci. Instr., 1935, **12**, 167).—The Pt electrode is sealed to a frame of Pyrex glass. C. W. G.

Large cloud chamber. G. Herzog (J. Sci. Instr., 1935, **12**, 153—159).—Internal dimensions are 50×25 cm. Straight tracks 50 cm. long have been obtained. C. W. G.

Electro-analysis with three electrodes. J. Guzmán and A. Sarabia (Anal. Fís. Quím., 1934, **32**, 275—279).—To obtain quant. adherent deposits of metal on the cathode, a third electrode is placed in the liquid, a const. p.d. being maintained between this electrode and the cathode. Experimental details for the determination of Cu are given. D. R. D.

Electro-endosmosis. VI. The " bubble-tube " method of measurement. F. Fairbrother and A. E. Stubbs (J.C.S., 1935, 527—529).—If the length of the bubble is > approx. 1·5 times the diameter, D, of the tube, the difference between the apparent velocity, U, of the liquid, as indicated by the bubble, and the true velocity is independent of the length of the bubble. When the thickness, d, of the film of liquid adhering to the walls of the tube is small compared with D, the fractional error, W, is given by $W=4d/D=\sqrt{(U\eta/\sigma)}$, approx., where η and σ are the viscosity and density, respectively, of the liquid. J. G. A. G.

Application of the buoyancy method in measuring the dielectric constant of electrolyte solutions. P. Mortier (Wis- en natuurk. Tijds., 1934, **7**, 36–43; Chem. Zentr., 1934, ii, 3650).—A modification of Preuner and Pungs' method (Physikal. Z., 1919, **20**, 543) applicable to dil. aq. KCl solutions is described. H. J. E.

Determination of conductivity of solutions of any salt content. F. Tödt (Chem.-Ztg., 1935, **59**, 357).—Apparatus which is applicable over a wide range of conductivity is described. E. S. H.

Large permanent magnet for the spectrographic study of β-rays. J. Surugue (J. Phys. Radium, 1935, [vii], **6**, 94—98). N. M. B.

Magnetic dilatometer. T. C. Richards (Iron and Steel Ind., 1935, **8**, 261—264). W. P. R.

Student's gas-density balance. C. C. Coffin (J. Chem. Educ., 1935, **12**, 142—143). L. S. T.

Ventilation of laboratory fume cupboards. A. Barbot (Bull. Soc. chim., 1935, [v], **2**, 666—668).—An electric fan is described. D. R. D.

Conicylindrical viscosimeter. M. Mooney and R. H. Ewart (Physics, 1934, **5**, 350—354).—A rotating cylinder viscosimeter is described. Ch. Abs. (*e*)

Support for crucibles. C. O. Harvey (Chem. and Ind., 1935, 391).—A no. of units, each consisting of a large and a small triangle, and made from fused SiO_2 tubing and Ni–Cr wire, are mounted on a common frame. A. L. R.

Physical methods in the chemical laboratory. XXIII. Physical methods of analysis. P. Wulff (Angew. Chem., 1935, **48**, 233—238; cf. A., 1934, 1324).—The influence of external factors on various physical methods of analysis, and their specificity, exactness, etc., are discussed in a general way. R. S.

Apparatus for the determination of minute quantities of radium, radon, and thoron in solids, liquids, and gases. R. D. Evans (Rev. Sci. Instr., 1935, [ii], **6**, 99—112).—A double ionisation chamber apparatus with photographic recording of ionisation current is described. Gaseous samples are examined directly; liquids are boiled in a flask fitted with a reflux condenser and Rn is swept out by a current of N_2 through the liquid; solids are first treated by a modified fusion furnace method. N. M. B.

Opening stoppered bottles. H. Schanz (Chem.-Ztg., 1935, **59**, 369).—A simple method of removing jammed stoppers is described. J. S. A.

Clamping glass tubing. J. A. V. Fairbrother (J. Sci. Instr., 1935, **12**, 169).—The glass tubing is held in a V-shaped slot in the end of a length of brass tubing by a wire or strip which passes around it and can be tightened by a screw and wing nut. C. W. G.

New alloy suitable for use in radium beam therapy. J. C. McLennan and C. J. Smithells (J. Sci. Instr., 1935, **12**, 159—160).—A W–Ni–Cu alloy of d 16·5 has a mean absorption coeff. of 0·83 cm.$^{-1}$ for hard γ-rays. C. W. G.

Gas washing device. R. Spence (J.S.C.I., 1935, **54**, 158T).—The gas bubbles up a spiral and discharges the washing liquid through a U-tube. The discharged liquid may be discarded, re-circulated, or pass into another washer arranged on the counter-current principle. R. S.

Low-pressure gas bubbler. E. W. Blank (J. Chem. Educ., 1935, **12**, 124).—A gas-absorption bubbler suitable for small vols. of gases at very low pressures is described. L. S. T.

Use of vacuum tubes in measurements. J. W. Horton (Electr. Eng., 1935, **54**, 93—102).—A bibliography and review. Ch. Abs. (*e*)

Plant for production of heavy water. W. G. Brown and A. F. Daggett (J. Chem. Physics, 1935, **3**, 216—218).—A more efficient electrolytic method for the production of heavy H_2O than previously used is described. The average fractionating factor, uncorr. for evaporation, is 8·6. The apparatus is explosion-proof. An additional purification stage is used to exclude N oxides. M. S. B.

Apparatus for filtering with avoidance of evaporation. H. de V. Robles (Chem. Weekblad, 1935, **32**, 255—256).—The liquid flows from a stoppered vessel, A, through a sintered glass filter into

another closed vessel, *B*. A by-pass carries the displaced air back from *B* into *A*. D. R. D.

Laboratory fractionating column. H. C. S. Snethlage (Chem. Weekblad, 1934, **31**, 748—749).—By the use of the simple apparatus described it is possible to separate 100% MeOH from mixtures containing up to 96% of H_2O, at the rate of 3 c.c. per min. H. F. G.

Quantitative extraction. A. G. Kuhlmann (Z. Unters. Lebensm., 1935, **69**, 221—227; cf. A., 1927, 1049).—Several modifications of the Soxhlet apparatus are described. E. C. S.

Extractor using a solution of volatile and non-volatile phases. A. J. Bailey (Science, 1935, **81**, 317).

High rotational speeds *in vacuo*. E. G. Pickels and J. W. Beams (Science, 1935, **81**, 342—343).—The adaptation of the air-driven ultracentrifuge for the production of high rotational speeds in a vac. is described. L. S. T.

Development of an air-driven ultracentrifuge. J. W. McBain and C. M. O'Sullivan (J. Amer. Chem. Soc., 1935, **57**, 780—781).—The air-driven spinning top has been developed into an ultracentrifuge for sedimentation analysis. E. S. H.

Vacuum evaporation and distillation. H. N. Naumann (Biochem. J., 1935, **29**, 994—997).—Improvements in the evaporation apparatus previously described (A., 1931, 191), whereby 5—30 litres of H_2O per hr. may be distilled at 20°, are detailed. H. D.

Visual demonstration of the evaporation of mercury. W. G. Leighton and P. A. Leighton (J. Chem. Educ., 1935, **12**, 139—142).—An open vessel containing Hg is placed between an A–Hg lamp and a screen coated with anthracene, uranyl sulphate, or willemite. Even at room temp. sufficient Hg vapour is swept out of the dish to cast shadows on the fluorescent background. This provides a sensitive method for detecting small amounts of Hg either metallic or combined rising from a heated sample. L. S. T.

Law of volatility. E. Montignie (Bull. Soc. chim., 1935, [v], **2**, 658—660).—Illustrations are given of the principle that, if two vapours are capable of reacting to produce a non-volatile substance, the reaction will be carried over in this direction. D. R. D.

Ramsay and helium. M. W. Travers (Nature, 1935, **135**, 619).—Historical. L. S. T.

Geochemistry.

Effect of wind on the concentration of carbon dioxide in the air. D. Szymkiewicz (Polish Agr. Forestal Ann., 1934, **33**, 13—22).—With increasing wind velocity from 0 to 0·8 and 1·2 m. per sec. the $[CO_2]$ decreases from 1·22 to 0·67 and 0·54 mg. per litre, respectively. Ch. Abs. (*e*)

Sea-water of the Puget Sound region. T. G. Thompson and R. J. Robinson (Proc. 5th Pacific Sci. Cong., 1933, 2101—2107).—Analytical data are recorded. Ch. Abs. (*e*)

Free ammonia, albuminoid nitrogen, and organic nitrogen (A) in the waters of the Puget Sound area, during the summers of 1931 and 1932, (B) in the waters of the Pacific Ocean off the coasts of Washington and Vancouver Island. R. J. Robinson and H. E. Wirth (J. cons. intern. expl. mer, 1934, 9, No. 1, 15—27; No. 2, 187—195).—Data are recorded. Ch. Abs. (*e*)

Rare gases. III. Helium–neon content of the ocean waters. W. D. Urry (J. Amer. Chem. Soc., 1935, **57**, 657—659; cf. A., 1933, 20, 1008).—The ratio to O_2 content and the variation with depth have been determined. E. S. H.

Ratio argon : nitrogen in natural gases. M. Geslin (Compt. rend., 1935, **200**, 1137—1139).—Natural gas from oil, petroleum, hot, or mineral springs is found to have a ratio $A : N_2 <$ for air. A study of the effect of the presence of fish, aquatic plants, Ra, etc. on the gases obtained from aquarium H_2O shows that the total combustible gases produced have a composition similar to CH_4, and that there is an increase in N_2, more rapid in presence of Ra, which probably originates in the destruction of animal and vegetable matter and hence there is a diminution in the ratio $A : N_2$. M. S. B.

Helium "beds." R. Wager (Naturwiss., 1935, **23**, 233—237).—The origin and location of sources of He are described. A. J. M.

Coal and natural oil in the Pittsburgh region. E. Linton (Science, 1935, **81**, 252).—The fact that oil and coal happen to occur in the latitude and longitude of the Pittsburgh region has no bearing on their origin (cf. this vol., 324). L. S. T.

Petroleum geology of Western Canada. A. J. Goodman (J. Inst. Petroleum Tech., 1935, **21**, 221—258).—Following a survey of the geological features of W. Canada, it is concluded that the greater part of the oil and gas probably originated in the Palæozoic limestones, although some source rocks may occur in the Mesozoics. C. C.

Effects of geophysical factors on the evolution of oil and coal. D. White (J. Inst. Petroleum Tech., 1935, **21**, 301—310).—Progressive carbonisation of coal and the evolution of petroleum (I) occur under geophysical influences (II) by processes equiv. to natural underground cracking, the pressure being of dominant importance. (I) is the product of sedimentary deposits of org. mother-substances of varying composition through biochemical and geochemical changes which take place underground in course of time under (II) and vary with the ratios of pressure, temp., and time. C. C.

***X*-Ray examination of the minerals of the earth's crust.** J. M. Bijvoet and W. Nieuwenkamp (Chem. Weekblad, 1934, **31**, 740—747).—A

detailed account is given of the insight which has been obtained into the structure of the naturally occurring complex silicates, and the conditions governing their deposition from the magma, by means of *X*-ray examination. H. F. G.

Optical study of emeralds and other minerals coloured by chromium. P. Vogel (Jahrb. Min., 1934, **A**, **68**, 401—438; Chem. Zentr., 1934, ii, 3369).—Emeralds from the chief sources may be differentiated by their absorption curves (I). Natural and artificial rubies have the same (I). Artificial rubies coloured with Cr have a different (I) from spinel coloured with Cr. Spinel with an excess of γ-Al_2O_3, coloured artificially with Cr_2O_3, has a different (I) from emerald. Synthetic corundum and spinel coloured green by V give similar (I), resembling that of spinel coloured with Cr_2O_3. Changes on tempering are discussed. H. J. E.

Constitution of stilpnomelane and stilpnochlorane. J. Holzner (Zentr. Min., 1934, **A**, 299—305; Chem. Zentr., 1934, ii, 3370).—From their constitution these substances are intermediate between the micas and the chlorites. The Ca in stilpnochlorane can be replaced in an exchange reaction by 2Tl. H. J. E.

Stainierite. L. de Leenheer (Natuurwetensch. Tijds., 1935, **17**, 44—48).—Macroscopic, optical, and *X*-ray examination shows that stainierite (Co_2O_3 72·19, Fe_2O_3 9·93, Al_2O_3 7·22, H_2O 10·66%; hardness 4·5, d 4·32) is heterogeneous and an impure form of Co_2O_3,H_2O. The dehydration curve is similar to that of mindigite. S. C.

Genetic relations of silver deposits and Keweenawan diabases in Ontario. E. S. Moore (Econ. Geol., 1934, **29**, 725—756).—Co and Ni arsenides and sulphides and native Ag are the typical ore minerals closely associated with diabase intrusions in the form of sills. The parent magma (I) contained Ag. The (I) of the diabase was the source of the ore solutions. Ch. Abs. (*e*)

Additional limonite types of galena and sphalerite derivation. R. Blanchard and P. F. Boswell (Econ. Geol., 1934, **29**, 671—690).—Two new types are described: the diamond-mesh boxwork, derived from steel galena, and the pyramidal, derived by pseudomorphic replacement of ordinary galena. Ch. Abs. (*e*)

Beryl–molybdenite deposit of Chaffee County, Colorado. K. K. Landes (Econ. Geol., 1934, **29**, 697—702).—The presence of beryl with molybdenite in the quartz vein indicates a deposition by hydrothermal solutions escaping from a deeper solidifying pegmatite. Ch. Abs. (*e*)

North Carolina talc deposits. J. L. Stuckey (J. Elisha Mitchell Sci. Soc., 1934, **50**, 41—42).—The talc deposits are associated with marble, and are probably formed by hot solutions from quartz-diorite dikes after metamorphism (I) of the sediments, and not by simple (I) of $MgCO_3$ in the original limestone. Ch. Abs. (*e*)

Differentiation in basalt lava, Island Magee, Co. Antrim. S. I. Tomkeieff (Geol. Mag., 1934, **71**, 501—512).—There is a rapid increase of MgO with depth. There has been a gravitational sinking of Mg-rich olivine, with the development of a border of iddingsite and chloropheite produced by contact with a hydrous Fe-enriched residual magma. Ch. Abs. (*e*)

Contaminated tonalites of Loch Awe, Argyll. S. R. Nockolds (Quart. J. Geol. Soc., 1934, **90**, 302—321).—The normal tonalite is contaminated by argillaceous, argillocalcareous, and calcareous xenoliths. The reaction process is discussed. Ch. Abs. (*e*)

Granite–schist contact in Stewart Island, New Zealand. G. J. Williams (Quart. J. Geol. Soc., 1934, **90**, 322—353).—The development of the minerals is described and discussed. Ch. Abs. (*e*)

Ultrabasic epidiorite from St. Catherine's, Loch Fyne. J. D. H. Wiseman (Geol. Mag., 1934, **71**, 425—427).—The rock is characterised by the absence of felspar, epidote, and sphene, and the present of penninite, and by the high MgO and Al_2O_3 and low alkali content. Ch. Abs. (*e*)

Secondary selenite crystals in tertiary strata in Texas. M. N. Broughton (Amer. Min., 1934, **19**, 466—473).—The occurrence is described. Its origin is discussed. Ch. Abs. (*e*)

Monticellite from Crestmore, California. R. S. Moehlman and F. A. Gonyer (Amer. Min., 1934, **19**, 474—476).—The composition is SiO_2 37·46, FeO 3·98, MnO 0·52, MgO 22·78, CaO 35·20, H_2O 0·15%. Physical data are recorded. The mineral is associated with garnet, and with diopside as an interstitial material. Ch. Abs. (*e*)

Petrology of the kaolin deposits near Anna, Illinois. R. E. Grim (Econ. Geol., 1934, **29**, 659—670).—The chief mineral is kaolinite. SiO_2, Fe oxide, and small amounts of kyanite, zircon, staurolite, tourmaline, ilmenite, leucoxene, rutile, sillimanite, epidote, anatase, and chloritic material are present. Ch. Abs. (*e*)

Kaolinite in Illinois coal. C. G. Ball (Econ. Geol., 1934, **29**, 767—776).—Chemical, optical, *X*-ray, and dehydration data are recorded for kaolinite found in desiccation cracks. Ch. Abs. (*e*)

Structures and textures of synthetic replacements in "open space." C. Schouten (Econ. Geol., 1934, **29**, 611—658).—Experiments are described on synthetic replacements in polished specimens of pure crystals, and mineral and crystal aggregates. The synthetic products resembled various types of natural ingrowth. Ch. Abs. (*e*)

Petrology of the Pennsylvanian shales and non-calcareous underclays associated with Illinois coals. II, III. R. E. Grim [with P. F. Kerr and O. W. Rees] (Bull. Amer. Ceram. Soc., 1935, **14**, 129—134, 170—176; cf. this vol., 603).—The results of petrographic, chemical, and *X*-ray examinations are recorded. J. A. S.

Mineral facies in metamorphic rocks. F. J. Turner (Amer. J. Sci., 1935, [v], **29**, 409—421).—The various assemblages of minerals that are stable under different conditions of temp. and pressure are considered. The presence of H_2O also has an im-

portant influence, and different cases are given by rising and falling temp. Green-schists, consisting of chlorite, epidote, and albite, are specially considered. L. J. S.

Layered peridotitic laccoliths in Newfoundland. E. Ingerson (Amer. J. Sci., 1935, [v], **29**, 422—440).—Large laccoliths in the Trout River area show at the base a thick zone of dunite and bronzite-peridotite, then a "critical zone" consisting of alternating layers of felspar-rich and olivine-rich rocks, and at the top a thinner zone of dunite and peridotite. Density determinations are given of the different types of rocks, and an explanation of the structure of the intrusion is offered. L. J. S.

Radium content of lavas, California. R. D. Evans and H. Williams (Amer. J. Sci., 1935, [v], **29**, 441—452).—The Ra content was determined for different types of rocks, basalt to dacite (SiO_2 51·13—66·65%) from the same area (Lassen volcanic, National Park). They gave Ra $0·33—0·80\times10^{-12}$ g. per g. The residual glass of the rock is richest in Ra, whilst felspar and biotite contain much less. There seems to be no connexion between the amount of Ra and the relative age of the lava flows. L. J. S.

Volume variation and modification of the lattice of sepiolites as a function of temperature. G. Migeon (Compt. rend., 1935, **200**, 946—949; cf. A., 1933, 369; this vol., 323, 468).—*X*-Ray spectral analysis shows that all sepiolites have a common characteristic initial lattice, but certain spacings vary from sample to sample. At 300°, dehydration occurs, followed by contraction, but no great change occurs in the crystal structure. At 460—750° slow and continuous loss of H_2O occurs, lattice changes setting in at 600°. At 750—820° H_2O is lost rapidly, considerable contraction occurs, and enstatite is formed. At 900—1000° dehydration is completed, contraction is very rapid, and the SiO_2 produced is in the form of cristobalite. J. W. S.

Sepiolite from Ampandrandava (Madagascar). H. Longchambon (Compt. rend., 1935, **200**, 949—951; cf. preceding abstract).—The fibrous structure of this sepiolite (sepiolite I) is attributed to chains of 4 Si and 11 O, to which Mg and OH ions are linked laterally. It loses 10·5% H_2O at 110° without change in crystal lattice. Change in the latter sets in at 300°, becomes rapid at 330—350°, and is complete at 500°. After heating at 500° the spacing along the fibre is unchanged but lateral spacings are reduced. This form (sepiolite II) is stable to 750° but above this temp. yields diffuse *X*-ray patterns with scarcely detectable periodicity along the fibre. At 780°, however, it yields the enstatite structure with the same longitudinal spacing as before. This passes into cristobalite at temp. varying from 850° to 1000°. Dilatometric and thermal analysis and study of the dehydration show that sepiolite I is a true Mg zeolite, whereas II has no zeolitic properties. Most of the H_2O is zeolitic, but part is necessary to the lattice structure. J. W. S.

Jarosite in tuff from Potosi, Bolivia. C. Milton (Amer. Min., 1935, **20**, 176—178).—A fine-grained siliceous tuff, containing 16% of jarosite, is described. L. S. T.

Lindgrenite, a new mineral. C. Palache (Amer. Min., 1935, **20**, 187).—Lindgrenite, $Cu_3MoO_4,Cu(OH)_2$, has $a:b:c=0·5941:1:0·5124$, β 92° 12′, and occurs as green crystals in veinlets in limonitic quartz in the Cu mine at Chuqicamata, Chile. L. S. T.

Age and distribution of pegmatites. K. L. Landes (Amer. Min., 1935, **20**, 81—105, 153—175).—Most of the known pegmatites are pre-Cambrian in age. A compilation of pegmatite occurrences throughout the world and maps are given. L. S. T.

Austinite, a new arsenate mineral, from Gold Hill, Utah. L. W. Staples (Amer. Min., 1935, **20**, 112—119).—Austinite, $CaZn(OH)AsO_4$, occurs as colourless orthorhombic crystals of prismatic habit and closely associated with adamite. The analysis is CaO 19·2, ZnO 32·5, As_2O_5 42·7, P_2O_5 0·1, H_2O 3·6, V_2O_5 0·0, residue 2·4, total 100·5%; $a:b:c=0·657:1:0·832$, n_α 1·759±0·003, n_β 1·763±0·003, n_γ 1·783±0·003, d 4·12 approx. L. S. T.

Contact metamorphic zone from the Little Belt Mountains, Montana. J. H. Taylor (Amer. Min., 1935, **20**, 120—128).—The petrography and paragenesis of the two silicate zones surrounding the igneous rock are described. The abundance of prehnite is a characteristic feature of the zone of dark silicates. Scawtite occurs in the zone of light silicates. L. S. T.

Anorthite from California. F. S. Miller (Amer. Min., 1935, **20**, 139—146).—The olivine-bearing phases of the San Marcos gabbro, San Luis Rey quadrangle, California, are composed predominantly of a plagioclase felspar which falls within the composition range of anorthite (94% An). Chemical analyses and the optical properties of this anorthite are given. L. S. T.

Celestite from Chittenango Fall, New York. N. W. Thibault (Amer. Min., 1935, **20**, 147—152).—The celestite, associated with much calcite, and smaller amounts of quartz and chalcedony, occurs as well-developed crystals lining irregular geodic cavities, and as massive and fibrous veins connecting the geodes. n_α 1·622, n_β 1·624, n_γ 1·632; d 3·939—3·968. A little Ca, but no Ba, isomorphously replaces the Sr. L. S. T.

Micro-diaclases in splinters of flint. Their importance in artificial coloration of micro-fossils and in particular of foraminifera. G. Deflandre (Compt. rend., 1935, **200**, 953—955).—When a polished splinter of flint is immersed for 2—4 hr. in a EtOH–H_2O solution of Dahlia-violet, washed, and examined microscopically, micro-diaclases appear. It is uncertain whether these are due to shock in obtaining the splinter or in polishing the sample or whether they exist in the body of the flint. Their importance in respect of the coloration of micro-fossils is pointed out. J. W. S.

Minerals from Csódi Mt., Hungary. R. Reichert and J. Erdélyi (Tsch. Min. Petr. Mitt., 1935, **46**, 237—255).—Descriptions with chemical analyses are given of zeolites (chabazite, analcime, and stilbite)

from cavities in andesite. The accompanying calcite is of various crystal habits. L. J. S.

Dissociation vapour pressure of sulphides and their order of deposition in magmatic ore deposits. E. KORDES (Tsch. Min. Petr. Mitt., 1935, 46, 256—288).—V.-p. curves (compiled from the lit.) for Zn, Cu, Fe, Ag, Pb, Bi, Sb, As, and Hg sulphides are in much the same order as that in which the corresponding sulphide minerals are deposited in hydrothermal veins, *i.e.*, the least volatile are deposited earlier. L. J. S.

Presence of rare alkaline metals in amazonites. J. M. TOLMATSCHEV and A. N. FILIPPOV (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 321—323).—Amazonites from various localities have been analysed spectrographically for their content of Li, Rb, Cs, Ga, and Be. Ilmenski Mountain amazonite (I) contains the largest % of Rb, 1—2%, with Rb : Cs approx. 20 : 1. The composition of amazonites corresponds with $(K,Rb,Na)_2Al_2Si_6O_{16}$. (I) contains 0·0015—0·002% of Sr, which is much > the amount producible by radioactive disintegration of Rb. It is suggested that the Sr is present to the extent of 30% as Sr^{87}. In (I) Sr : Ca=approx. 1 : 100, and Y and Cu are $\not>$ 0·001%, so that the blue colour cannot be due to the latter. Traces of Pb are present in all amazonites. R. S. B.

Linnæite group of cobalt–nickel–iron–copper sulphides. W. A. TARR (Amer. Min., 1935, 20, 69—80).—Available analyses are discussed for linnæite, carrollite, sychnodymite, siegenite, violarite, and polydymite. They should be represented by the general formula $R''R'''_2S_4$ where R″ is $Co^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Cu^{\cdot\cdot}$, and $Fe^{\cdot\cdot}$ and R‴ $Co^{\cdot\cdot\cdot}$, $Ni^{\cdot\cdot\cdot}$, and $Fe^{\cdot\cdot\cdot}$. The Co, Ni, Fe, and $Cu^{\cdot\cdot}$ are isomorphous. The name "carrollite," $CuCo_2S_4$, is preferred for those minerals rich in Cu, whilst that of "sychnodymite" should be discarded. *X*-Ray investigations of all these members, except violarite, show that they possess the spinel structure type. L. S. T.

Magnetite cementing certain ore conglomerates of the Mesabi range. J. W. GRUNER (Econ. Geol., 1934, 29, 757—760).—The magnetite (FeO 30·94, Fe_2O_3 69·05%, MnO trace) was apparently of hydrothermal origin. CH. ABS. (*e*)

Recent vulcanism and the formation of iron ores. F. BEHREND (Z. deut. geol. Ges., 1934, 86, 360—367; Chem. Zentr., 1934, ii, 3370).—A description and discussion of Fe deposits in Santorin. H. J. E.

Organic minerals. IV. Chlorophyll and hæmin derivatives in rocks, petroleums, coals, and phosphorites. A. TREIBS (Annalen, 1935, 517, 172—196; cf. A., 1934, 387, 629).—In 22 of 27 specimens of petroleum examined, porphyrins (I) were immediately detected spectroscopically. In all cases deoxophylloerythroætioporphyrin predominated, other (I) being similar to and in similar amount to those already recorded (*loc. cit.*). In an individual oil-shale the proportion of complex was sufficient to permit its isolation and identification synthetically. It was thus shown to be a V compound, but the prep. by use of VCl_4 and NaOAc probably involves reduction of V^{IV}. The composition of the complex is not fully established, the analytical vals. lying between those of a VO [or $V(OH)_2$] and VO_2 derivative. The salts are stable towards conc. HCl and are only slowly decomposed by conc. H_2SO_4. They can be reduced to complex leuco-compounds which are stable to acid but readily oxidised by air to the initial substances. The presence in petroleums and bituminous extracts of a Fe^{II} complex, apparently derived from mesoætioporphyrin and characterised by complete stability to air, is also established. All (I) previously detected in minerals could be observed in coals whilst in 3 samples a material closely resembling deuteroætioporphyrin and the corresponding acid porphyrin were observed. Phosphorites contain the same (I) as petroleums and oil-shales but the amounts of acidic (I) exceed those of ætioporphyrins. In an individual case a material with the properties of mesoporphyrin was detected. Coproporphyrin and a spectroscopic analogue of hæmatoporphyrin were present in guano and (I) in asphalt. It is considered that petroleums, bitumens, coals, and phosphorites cannot have been subjected to a temp. above 200°. The formation of phosphorites from guano is highly improbable and the participation of green plants in their production is suggested. The occurrence of (I) in complex union with V or Fe^{II} is a secondary phenomenon. Less firmly bound elements are displaced, thus accounting for the remarkable accumulation of V in the ashes of petroleums and asphalts. H. W.

Organic Chemistry.

Principles of the co-ordination theory and some applications to organic chemistry. G. URBAIN (Bull. Soc. chim., 1935, [v], 2, 555—569).—A lecture.

General mechanism of fission of carbon chains. R. CRIEGEE (Ber., 1935, 68, [*B*], 665—668).—The general hypothesis is that if 2 atoms or groups in the αδ-position in a mol. are removed, the remainder undergoes fission between the β and γ atoms. Examples cited in favour of this view are (1) the formation of ethylenes by the cautious removal of metals from αδ-dialkali-substituted butanes; (2) the production of C_2H_4 from $(\cdot CH_2\cdot CH_2I)_2$, (3) the fission of glycols by $Pb(OAc)_4$, (4) Tiffeneau's interpretation of the pinacolin transformation through αγ-diradicals, (5) the conversion of β-OH-acids in which α-H atoms are replaced by alkyl into CO_2 and alkylenes, $OH\cdot CHMe\cdot CMe_2\cdot CO_2H \longrightarrow \cdot CHMe\cdot CMe_2\cdot CO\cdot O\cdot \longrightarrow CHMe{:}CMe_2 + CO_2$, (6) the cracking of saturated hydrocarbons. H. W.

Thermal decomposition of hydrocarbons. P. P. BORISOV, E. M. SCHACHNAZAROVA, and E. I. MARGOLIS (J. Gen. Chem. Russ., 1934, 4, 1385—1389).—Hexane, *cyclo*-pentane, -hexane, and -hexene, decahydronaphthalene, and C_6H_6 give rise to H_2 and

saturated hydrocarbons when heated at 1200°; except in the case of C_6H_6 the content of unsaturated hydrocarbons rises with fall in temp. R. T.

Relation between the structure of hydrocarbons and their miscibility with selective solvents.—See this vol., 694.

Wurtz synthesis. W. Hückel, A. Kraemer, and F. Thiele (J. pr. Chem., 1935, [ii], **142**, 207—217).—The following are typical % yields (of the theoretical) of products obtained in Wurtz syntheses using Na or Na–K in xylene as a solvent (H_2 atm.). Saturated hydrocarbons were determined by isolation and/or explosion with O_2, and unsaturated by catalytic reduction and by absorption in Br–H_2O: EtCl gives C_2H_4 5·5, C_2H_6 32, C_4H_{10} 12, EtBr giving 3, 33·5, and 27%, respectively. Pr$^\alpha$Cl affords C_3H_8 21·5, C_3H_6 10·5, C_6H_{14} 23, Pr$^\alpha$Br giving 8, 6, and 65%, respectively; Pr$^\beta$Cl, C_3H_8 40, C_3H_6 18·5, Pr$^\beta$Br giving 45 and 10%, respectively; MeBr gives C_2H_6 12·5%. MeBr+EtBr afford C_2H_6 7, C_2H_4 9·5, C_3H_8 15%, C_4H_{10} 28%; MeBr+Pr$^\alpha$Br give C_2H_6 3, C_3H_6 9·4, C_4H_{10} 7·5, C_6H_{14} 44%; MeBr+Pr$^\beta$Br, C_2H_6 15, C_3H_6 15, and $CHMe_3$ 43%. Bromides react more readily than chlorides, but the results are not always reproducible.

J. W. B.

Highly-polymerised compounds. CXI. Measurements of viscosity of paraffins. H. Staudinger and F. Staiger (Ber., 1925, **68**, [*B*], 707—726).—For substances with spherical mols. the vals. of $\eta_{sp.}/c$ are const. over a very wide range of concn., whereas in the case of thread mols. this is the case only in dil. sol solution. In a paraffin such as ethylhentriacontane a 20% solution is intermediate between sol and gel; the vals. of $\eta_{sp.}/c$ are const. up to 5%, whereas in 8·4% solution discrepancies become obvious. With *n*- and *iso*-paraffins y (sp. viscosity of a chain link) $=1{\cdot}5\times10^{-3}$ in CCl_4 and $1{\cdot}3\times10^{-3}$ in C_6H_6. With rising temp. $\eta_{sp.}$ diminishes regularly, and at 60° is 6—15% < at 20°. Similar relationships between $\eta_{sp.}$ and chain length are found with *n*-hexacontane as with simpler members of the series. With myristone and stearone (I) the vals. of y are approx. identical with those found with hydrocarbons. Measurements of the viscosity of paraffins in various solvents and mixtures of solvents are recorded, and the question of solvation is discussed. Comparative determinations of the mol. wt. of fractions of a hard paraffin by measurement of $\eta_{sp.}$ in PhCl and cryoscopically in $C_{10}H_8$ and camphor show that the correct relationships between $\eta_{sp.}$ and chain length are shown only when such mixtures are as homogeneous as possible. σ-*Ethylidenepentatriacontane*, m.p. 21·5° [ozonised to AcOH and (I)], is obtained by the action of a large excess of MgEtI on (I) and distillation of the product in vac.; it is converted by H_2 at 150°/80 atm. in presence of *cyclo*hexane and Ni into σ-*ethylpentatriacontane*, m.p. 39°. H. W.

Titrimetric determination of iodine values [of unsaturated hydrocarbons] with bromine vapour. E. Rossmann (Angew. Chem., 1935, **48**, 223—226).—A weighed quantity of Br sealed in a thin glass bulb is introduced into a round-bottomed flask fitted with a funnel having a stopcock and containing the substance (I) to be tested. The flask is evacuated and (I) distributed around the flask wall, the Br bulb broken, and the whole placed in the dark. For substances containing one double linking a 200% excess of Br allows interaction to be complete in 10 min. If 3 double linkings are present 400—500% excess allows completion in the same time. Excess of Br is titrated with As_2O_3 after KBr solution, with CCl_4 if necessary, has been added or KI may be added and the I titrated. Excess of Br has no influence on results, blank tests are unnecessary, and no substitution reactions can occur. The method appears universally applicable. C. I.

Reaction between oxygen and Δ$^\beta$-butene. H. J. Lucas, A. N. Prater, and R. E. Morris (J. Amer. Chem. Soc., 1935, **57**, 723—727).—Δ$^\beta$-Butene and O_2 at 375—490° give much MeCHO, some butadiene, and (at 490°) CH_4, with a little glyoxal (or CHO·CH_2·OH), an olefine oxide, and acid (or acids), and peroxide. Absence of Ac_2, CHMeAc·OH, and COMeEt shows that oxidation does not proceed by hydroxylation. A possible reaction mechanism, involving formation of βγ-dioxidobutane, is proposed. R. S. C.

Hydrocarbons C_8H_{14} formed by the interaction of crotonyl bromide and its magnesium derivative. R. Lespieau and P. Heitzmann (Compt. rend., 1935, **200**, 1077—1080; cf. Braun *et al.*, A., 1923, i, 286).—Crotonyl bromide and Mg yield a mixture of hydrocarbons from which (·CH_2·CH:CHMe)$_2$ (I), b.p. 122—125° (*tetrabromide*, m.p. 184—184·5°), CHMe:CH·CH_2·CHMe·CH:CH_2 (II), b.p. 110—111° (*di-iodide*, m.p. 155—156°), and a trace of (·CHMe·CH·CH_2)$_2$ (III), b.p. 100° (*tetraiodide*, decomp. 100°), have been separated. Hydrogenation of (I) gives octane and of (II) gives methylheptane. Raman spectra indicate that (I) is a mixture of *cis*- and *trans*-forms. F. N. W.

Synthesis of tetratriacontadiene. Its properties with special reference to oiliness. M. V. Dover and C. J. Helmers (Ind. Eng. Chem., 1935, **27**, 455—458).—Electrolysis (conditions described) of oleic acid in EtOH–H_2O containing K_2CO_3 at 50—60° affords tetratriacontadiene (I), m.p. 20·5—21° (purification described), which distils at 120—170°/1—1·5 mm. to give a liquid (II) and a viscous residue (III). (I) can be reduced (H_2–PtO_2–$FeSO_4$) and absorbs I nearly quantitatively. (II) probably contains decomp. products, and (III) polymerides, of (I). J. L. D.

Iodo-silver benzoate complex [as] iodinating agent; probable structure of the complex. C. Prévost (Compt. rend., 1935, **200**, 942—944).—With CPh:CH, the complex AgI$(OBz)_2$ (A., 1933, 711) yields CPh:CI, AgOBz, and BzOH; with C_2H_2, it gives CH:CI and [CI:]$_2$. The structure $[Ag(OBz)_2]^-I^+$ is proposed. E. W. W.

Isomerisation of hydrocarbons. I. Chlorination of hexane and octane isomerides with antimony pentachloride as a method for their determination. B. L. Moldavski and S. E. Livschitz (Compt. rend. Acad. Sci. U.R.S.S., 1935, **1**, 507—513).—The amount of chlorination of *iso*-C_6H_{14} or -C_8H_{18} (I) by $SbCl_5$ (12 mols.) (cf. Schaarschmidt, B., 1932, 493) in CCl_4 or $CHCl_3$ depends on the [$SbCl_5$], but, within the limits of experimental error, not on the

structure of (I). Traces of H_2O greatly inhibit the reaction, but in dry solution chlorination of (I) is readily effected (C_6H_{14} faster than C_8H_{18}) with 0·1*N*-$SbCl_5$ in CCl_4 at room temp., conditions under which the corresponding *n*-hydrocarbons (II) are unaffected: $CR'R''MeCl-HCl \longrightarrow CR'R''{:}CH_2+SbCl_5 \longrightarrow CR'R''Cl{\cdot}CH_2Cl$. A trustworthy method for the determination of (I) in presence of (II) is described. After interaction with a known vol. of standard $SbCl_5$–$CHCl_3$ for 2—6 hr., dil. HCl is added, and the excess of $SbCl_5$ is determined by titration with 0·1*N*-$KBrO_3$ (Me-orange). Comparison of the titre with that of a control experiment using a solution of (I) in (II) of known concn. enables the proportion of (II) to be determined. The results (examples given) are satisfactory even if the [(I)] is only 10%. J. W. B.

Widmark's alcohol determination. C. A. Meier and O. Wyler (Arbeitsphysiol., 1934, 7, 528—535; Chem. Zentr., 1934, ii, 3997).—Details of procedure are discussed. J. S. A.

New methods of application of calcium carbide. L. Kazarjan (J. Gen. Chem. Russ., 1934, 4, 1347—1352).—$COMe_2$ (I) (1 mol.) is added to an Et_2O suspension of a 1 : 1-mol. mixture of KOH and CaC_2 (24 hr.; 0°), H_2O at 0° is added, the aq. layer is saturated with NaCl and Et_2O-extracted, and the combined Et_2O extracts are distilled, when $CH{:}C{\cdot}CMe_2{\cdot}OH$ (II) is obtained in 70% yield. $(OH{\cdot}CMe_2{\cdot}C{:})_2$ is obtained similarly (74% yield) when 2 mols. of (I) are taken. The reactions involved are $CaC_2+KOH \longrightarrow CK{:}C{\cdot}CaOH$ (III); $(III)+(I) \longrightarrow OK{\cdot}CMe_2{\cdot}C{:}C{\cdot}CaOH \longrightarrow CK{:}C{\cdot}CMe_2{\cdot}O{\cdot}CaOH \xrightarrow{H_2O} (II)$. R. T.

Compounds of oxyhalides with unsaturated substances. II. Reaction of nitrogen iodide with acids and alcohols in presence of olefines. A. A. Petrov (J. Gen. Chem. Russ., 1934, 4, 1458—1463).—The following esters of β-iodo-γ-hydroxybutane (I) have been prepared by adding NI_3 to a mixture of CHMe:CHMe (II) and the appropriate acid at −10°: *formate*, b.p. 72·5°/11 mm., *propionate*, b.p. 97—98·5°/15 mm., iso*butyrate*, b.p. 101—109°/15 mm., iso*valerate*, b.p. 101—104°/10 mm. The ethers of (I) formerly described (this vol., 605) can also be obtained by conducting the above reaction in presence of the appropriate alcohol: $3R{\cdot}CO_2H+NI_3 \longrightarrow NH_3+3R{\cdot}CO_2I$; $R{\cdot}CO_2I+R'OH \longrightarrow R{\cdot}CO_2H+R'OI$; $R'OI+(II) \longrightarrow OR'{\cdot}CHMe{:}CHMeI$. R. T.

Symmetrical amyl, hexyl, heptyl, and butyl sulphates. M. Levaillant (Compt. rend., 1935, 200, 940—942; cf. A., 1933, 1274).—Amyl chlorosulphonate and sulphite react (+$ZnCl_2$ at 85°) to form *amyl sulphate*, m.p. 13—13·5°, b.p. 128—130°/3 mm. *n*-$C_6H_{13}{\cdot}OH$ with SO_2Cl_2 and $SOCl_2$ respectively yields *hexyl chlorosulphonate*, b.p. 81°/2·5 mm., and *sulphite*, b.p. 156°/11 mm., which react to form *hexyl sulphate*. n-*Heptyl chlorosulphonate*, b.p. 90—92°/3 mm., and *sulphite* give *heptyl sulphate*, m.p. 13°. The last, and Bu_2SO_4, are also prepared from the alcohols and SO_2Cl_2, with the sulphites, without isolating the chlorosulphonates. E. W. W.

Esters of thiosulphurous acid, $H_2S_2O_2$. H. Stamm (Ber., 1935, 68, [*B*], 673—676).—The greenish-yellow $Me_2S_2O_2$ obtained according to Meuwsen (this vol., 326) contains about 2·5% of S_2Cl_2. Mixtures of colourless $Me_2S_2O_2$ with 2·5% of S_2Cl_2 have the same colour and give all the chemical reactions, which are similarly exhibited by a solution of pure S_2Cl_2 in anhyd. Et_2O. $Et_2S_2O_2$ and S_2Cl_2 are not completely separable from one another by distillation under diminished pressure. H. W.

Catalytic preparation of butyl acetate and butyl butyrate.—See B., 1935, 395.

Addition of hydrogen sulphide and mercaptans to alkylene oxides. C. D. Nenitzescu and N. Scărlătesci (Ber., 1935, 68, [*B*], 587—591).—When passed through a flask fitted with a Raschig column H_2S and $(CH_2)_2O$ give a 90·3% yield of $S(CH_2{\cdot}CH_2{\cdot}OH)_2$ if the rings have been moistened with the product; otherwise reaction does not appear to occur. $OH{\cdot}CH_2{\cdot}CH_2{\cdot}SEt$ is obtained similarly from $(CH_2)_2O$ and EtSH. PhSH and $(CH_2)_2O$ in presence of active C at room temp. afford *Ph* β-*hydroxyethyl sulphide*, whilst at 90° *cyclo*hexene oxide (I) and PrSH yield *Pr*$^\alpha$ 2-*hydroxy*-1-cyclo*hexyl sulphide*, b.p. 96—97°/3 mm. (I) is transformed by PhSH and active C at 130—135° into *Ph* 2-*hydroxy*-1-cyclo*hexyl sulphide*, b.p. 148—149°/4 mm., oxidised by H_2O_2 in AcOH to *Ph* 2-*hydroxy*-1-cyclo*hexyl sulphone*, m.p. 109°. CH_2Ph 2-*hydroxy*-1-cyclo*hexyl sulphide* has b.p. 158—160°/3 mm. Epichlorohydrin (II) affords *Et* (III), b.p. 114—115°/16 mm., *Pr*, b.p. 95°/4 mm., *Ph*, b.p. 141°/4 mm. (corresponding *sulphone*, m.p. 72°), and CH_2Ph, b.p. 154—156°/4 mm., γ-*chloro*-β-*hydroxypropyl sulphide*. Addition of (III) to 40% aq. KOH yields *Et* βγ-*oxido*-n-*propyl sulphide* (IV), b.p. 67°/15 mm., also obtained by addition of (II) to EtSH in KOH. When heated with $NHEt_2$ at 140° (IV) yields *Et* γ-*diethylamino*-β-*hydroxy*-n-*propyl sulphide*, b.p. 131°/17 mm.; *Et* γ-1-*piperidino*-β-*hydroxy*-n-*propyl sulphide*, b.p. 130—131°/4 mm., is prepared similarly. (IV) and MeI in EtOH at room temp. yield *methylethyl*-βγ-*oxido*-n-*propylsulphonium iodide*. H_2S and (II) afford non-distillable γγ′-*dichloro*-ββ′-*dihydroxydipropyl sulphide*. H. W.

Mechanism of condensation of carbonyl compounds by means of alkali metals. G. V. Tschelincev (Compt. rend. Acad. Sci. U.R.S.S., 1935, 1, 393—397).—The following scheme is proposed for ester condensations: $EtOAc+CH_2Na{\cdot}CO_2Et \rightleftharpoons ONa{\cdot}CMe(OEt){\cdot}CH_2{\cdot}CO_2Et \rightleftharpoons COMe{\cdot}CH_2{\cdot}CO_2Et+NaOEt \rightleftharpoons ONa{\cdot}CMe{:}CH{\cdot}CO_2Et+EtOH$ (cf. A., 1934, 868). This correlates this condensation with the synthesis of carbonyl compounds by means of organometallic compounds of Zn, Mg, and Na (*i.e.*, $R{\cdot}CO_2Et+MgR'I \rightleftharpoons MgI{\cdot}O{\cdot}CRR'{\cdot}OEt$). The scheme also explains the condensation of aldehydes and esters with α-Cl-substituted esters, ketones, etc. (*i.e.*, the formation of $\overset{CHR}{O}\!\!>\!\!CH{\cdot}CO_2Et$ from R·CHO and $CHClNa{\cdot}CO_2Et$). The scheme is applied to the explanation of many condensations previously unexplained or explained with difficulty, and to the determination of the factors which control the direc-

tion of the reaction between two different reactants which can also condense with themselves. H. G. M.

Rare earths.—See this vol., 714.

Indium salts of organic acids. J. B. EKELEY and W. W. JOHNSON (J. Amer. Chem. Soc., 1935, 57, 773—774).—Basic *salts*, $InX_2 \cdot OH$, are prepared, in which X is $EtCO_2$, $Pr^{\alpha}CO_2$, $CCl_3 \cdot CO_2$, BzO, *o*-, *m*-, and *p*-$C_6H_4Me \cdot CO_2$. R. S. C.

Constitution of formic acid and formates. T. R. SESHADRI (Current Sci., 1935, 3, 353—354).—The evidence in favour of the idea that the exceptional behaviour of HCO_2H, as compared with that of its homologues, is due to the presence of CHO is discussed. F. N. W.

Action of nitric acid on dipropionyl peroxide. F. FICHTER and H. BUESS (Helv. Chim. Acta, 1935, 18, 549—555; cf. this vol., 472).—The nitrogenous esters obtained during electrolysis (I) of mixtures (II) of nitrate and propionate (III) are exclusively nitrates; nitrites or nitrite-nitrates are not present. The action of anhyd. fuming HNO_3 on dipropionyl peroxide yields $EtNO_3$ and $EtCO_2Et$, also obtained by (I); in addition $EtNO_2$ is produced. C_2H_4 is formed during electrolysis of (II) or (III). Hypotheses concerning the formation of butane derivatives during electrolysis are not supported experimentally. H. W.

Highly-polymerised compounds. CXII. Determination of molecular form by viscosity measurements. H. STAUDINGER and H. SCHWALENSTÖCKER (Ber., 1935, 68, [*B*], 727—749).—Examination is made of the possibility of determining the mol. form of a large series of aliphatic compounds by measurement of the viscosity of their solutions and of correlating the results with other physical properties of the substances. In CCl_4 and C_6H_6 the vals. adopted for γ are $1{\cdot}5 \times 10^{-3}$ and $1{\cdot}3 \times 10^{-3}$, respectively. The sp. viscosity of lauric, myristic, and palmitic acids (c=1·4) is the same as that of their respective anhydrides, which agrees with the view that the anhydride mols. are extended and the acids are bimol. and finds confirmation in the respective m.p. With *methylene myristate*, from the anhydride and $(CH_2O)_n$ in presence of a little $ZnCl_2$ at 100°, the calc. and observed vals. of $\eta_{sp.}$ agree within experimental error. *Tetramethylene dilaurate*, m.p. 45·5°, *dimyristate*, m.p. 55·0°, and *dipalmitate*, m.p. 63·0°, have the straight chain $Me \cdot [CH_2]_x \cdot CO \cdot O \cdot [CH_2]_4 \cdot O \cdot CO \cdot [CH_2]_x Me$. In CCl_4 and C_6H_6 the vals. of $\eta_{sp.}$ of ethylene laurate, m.p. 52·0°, myristate, m.p. 63·0°, and palmitate, m.p. 70·5°, are about $4{\cdot}0 \times 10^{-3}$ < calc. for a straight chain and structures are discussed wherein the chain length is shortened by about 2 links. A similar anomaly is observed with *αβ-propylene dilaurate*, m.p. 35·0°, *dimyristate*, m.p. 41·5°, and *dipalmitate*, m.p. 52·5—54·5°, and with *αγ-butylene dilaurate*, m.p. about 16·5°, *dimyristate*, m.p. 29·5—31·0°, and *dipalmitate*, m.p. 39·0—40°, and to a smaller extent with β-n-*butoxyethyl laurate*, m.p. about −4° to −3°, *myristate*, m.p. about 7°, and *palmitate*, m.p. 18·5°. *Nonyl*, m.p. 25·5°, and *cetyl*, m.p. 56—57°, *oxalate*, *nonyl*, b.p. 176°/0·14 mm., m.p. 21—21·5°, and *cetyl*, m.p. 55·5—56°, *succinate*, and *nonyl*, m.p. 17—18·5°, and *cetyl adipate*, m.p. 53°, have extended mols., whereas possible shortening of the chain occurs with *nonyl*, b.p. 167°/0·18 mm., m.p. about 0·5—1·5°, and *cetyl malonate*, m.p. 50·5°. Trilaurin, trimyristin, and tripalmitin appear to have extended mols. and the viscosity seems to be influenced by the large side-chain. H. W.

Action of atomic hydrogen on oleic acid and paraffin oil. H. KROEPELIN and E. VOGEL [with H. PFEIFFER] (Ber., 1935, 68, [*B*], 684—688).—Exposure of thin films of oleic acid (I) to at. H leads to the formation of stearic acid, a thin skin on the surface of the product which is not observed if O is completely absent, and a brown sticky polymerisate (II). The mean mol. wt. of (II) in boiling C_6H_6 is 1000—2000, depending greatly on the concn. 54% of the original double linkings are hydrogenated. CO_2H is partly reduced. (II) appears to contain an unassigned excess of O, but its formation is observed even when O is completely absent. It is considered that polymerisation is preceded by radical formation, $C_nH_{2n+2} + H = C_nH_{2n+1} + H_2$, and that the double linking of (I) is not fundamental for its polymerisation. In confirmation, paraffin oil when treated with at. H in complete absence of O shows increase of mean mol. wt. from 380 to 535; since the I val. increases from 0·2 to 14·0, double linkings are developed. In presence of a trace of O thin skins are formed (C 74·93, H 10·26, O 14·8%). Reduction of (I) by at. H occurs to only a moderate extent, whilst Et oleate does not appear to be reduced. H. W.

Velocity of saponification of some simple triglycerides by ethyl-alcoholic potash.—See *this* vol., 709.

Synthesis of "alkeines" derived from α-alkoxypropionic acid. Z. RODEWALD and E. PŁAŻEK (Rocz. Chem., 1935, 15, 81—87).—$CHMeBr \cdot CO_2Me$ and NaOMe in MeOH are boiled for 3 hr., NaOH is added, the solution is heated for a further 30 min., and $OMe \cdot CHMe \cdot CO_2H$ (I) is extracted from the product. The corresponding *Et* (II), b.p. 99°/16 mm. (*chloride*, b.p. 54—58°/60 mm.), and *Pr* (III) *ether*, b.p. 105°/17 mm. (*chloride*, b.p. 68°/45 mm.), are prepared analogously. The *tropyl* ester of (I), b.p. 160°/24 mm. (*picrate*, m.p. 187°; *picrolonate*, m.p. 237°), of (II), b.p. 98—100°/0·2—0·3 mm. [*picrate*, m.p. 182—183°; *picrolonate*, m.p. 193°; *methiodide*, m.p. 255° (decomp.)], and of (III), b.p. 115°/0·3 mm. (*picrate*, m.p. 158°; *picrolonate*, m.p. 175°), are obtained by passing dry HCl through a fused mixture of tropine and the appropriate acid at 110° (3 hr.). The *chloride*, b.p. 40°/60 mm., of (I) and $NMe_2 \cdot CH_2 \cdot CH_2 \cdot OH$ in Et_2O afford β-*dimethylaminoethyl* α-*methoxypropionate*, b.p. 86—88°/16 mm. (*picrate* of methiodide, m.p. 64°); the corresponding *esters* of (II), b.p. 95—96°/16 mm., and of (III), b.p. 112—115°/17 mm., are prepared similarly. R. T.

Ether-like compounds. XV. Ether-lactones with five-membered ring. M. H. PALOMAA, E. J. SALMI, and L. WALLIN [with T. A. SIITONEN] (Ber., 1935, 68, [*B*], 609—618).—The following esters are obtained by heating the requisite α-OH-acid with the

aldehyde or ketone in presence of p-$C_6H_4Me{\cdot}SO_3H$ as catalyst and, if necessary, Na_2SO_4 as absorbent of H_2O. Methylene lactate (I), b.p. 152—153°/758 mm., methylene α-hydroxy*iso*butyrate (II), b.p. 149·5—150°/755 mm., *methylene α-hydroxy-α-methyl*-n-*butyrate* (III), b.p. 165·5—166·5°/762 mm., and *methylene α-hydroxy-α-ethyl*-n-*butyrate* (IV), b.p. 68—69·5°/8—9 mm. Hydrolysis of (I), (II), (III), and (IV) by acid is an ester hydrolysis; the temp. coeffs. are similar to those of ester hydrolysis and increasing alkylation depresses the reactivity. Ethylidene lactate (V), b.p. 154—155°/769 mm., α-hydroxy-*iso*butyrate (VI), b.p. 151—152°/758 mm., *α-hydroxy-α-methyl*-n-*butyrate*, (VII), b.p. 169—170°/763 mm., and *α-hydroxy-α-ethyl*-n-*butyrate* (VIII), b.p. 69·5—72°/8—10 mm., are described. In 0·1*N*-HCl hydrolysis of (V) is mainly due to H_2O, to which about half the total change is ascribed in the cases of (VI), (VII), and (VIII). Acid hydrolysis of (I)—(VIII) is greatly diminished by increased alkylation of the acidic component and this is even more the case with aq. hydrolysis. The temp. coeffs. of acid hydrolysis of (V)—(VIII) approximate to the vals. of acetal hydrolysis as the reactivity of the acidic component is depressed by alkylation. *Propylidene*, b.p. 68—69°/19—20 mm., and iso*butylidene lactate*, b.p. 68—69·5°/14 mm., have been obtained. H. W.

Phospho-*l*-lactic acid. T. Wagner-Jauregg (Ber., 1935, **68**, [*B*], 670—673).—*l*(+)-Lactic acid (I) in C_5H_5N is converted by $POCl_3$ into phospho-*l*-lactic acid (II) isolated as the *salt* $C_6H_8O_{12}P_2Ba_3,4H_2O$, less sol. in hot than in cold H_2O. (II), as Na_3 or K_3 salt, has $[\alpha]_D$ −9·74° in H_2O. (II) is about as readily hydrolysed as phosphoglyceric acid by HCl at 122° but is much more resistant to de-phosphorylating enzymes. Methylene-blue in presence of lactic dehydrase from *B. coli* in vac. is decolorised by (I) but not by (II); (II) is therefore not an intermediate product of the dehydrogenation of (I). H. W.

Synthesis of *enol*-phosphopyruvic acid. W. Kiessling (Ber., 1935, **68**, [*B*], 597—601).—Condensation of $AcCO_2H$ with $POCl_3$ in quinoline at 40—60° affords (10% yield) *enol*-phosphopyruvic acid (I), $CH_2{:}C(O{\cdot}PO_3H_2){\cdot}CO_2H$, with large amounts of complex by-products, usually free from P. (I) yields a Ag–Ba salt (II), does not give a ppt. with $(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2$, yields CHI_3 with IO' with loss of H_3PO_4, and is immediately decomposed by Hg salts into $AcCO_2H$ and H_3PO_4. (II) is catalytically hydrogenated (Pd) to phospholactic acid. (I) is therefore identical with the natural acid (Lohmann *et al.*, A., 1934, 1261). H. W.

Oxidation of ethyl hydrogen malonate by potassium persulphate. F. Fichter and J. Heer (Helv. Chim. Acta, 1935, **18**, 704—709).—Oxidation of $CO_2Et{\cdot}CH_2{\cdot}CO_2K$ (I) with $K_2S_2O_8$ gives $(\cdot CH_2{\cdot}CO_2Et)_2$ (II), showing that the production of (II) from (I) by electrolysis is due to electrochemical oxidation and not to simple discharge. The reaction also affords AcOH and EtOAc but, under the experimental conditions, $(\cdot CH_2{\cdot}CO_2H)_2$ cannot be formed from AcOH. The Crum Brown–Walker and Kolbe syntheses of hydrocarbons are due to electrochemical oxidation. H. W.

Preparation of organic compounds containing deuterium. Dideuteromalonic deuteracid and trideuteracetic deuteracid. C. L. Wilson (J.C.S., 1935, 492—494).—C_3O_2 and D_2O in dry C_6H_6 give *dideuteromalonic deuteracid*, $CD_2(CO_2D)_2$, m.p. 128—130° (decomp.), no interchange of H and D in the C_6H_6 occurring. Decomp. at 140—150° gives *trideuteracetic deuteracid* (I), $CD_3{\cdot}CO_2D$, m.p. 15·75°, for which v.p. are recorded between 20·0° (12·4 mm.) and 100·0° (437·9 mm.). (I) is more volatile than "light" AcOH, in agreement with Lewis' views on the co-ordination of H and D. R. S. C.

Autoxidation of methyl sorbate. P. Heinänen (Suomen Kem., 1935, **8**, B, 5—6).—The product of autoxidation of Me sorbate is the γδ-peroxide, which decomposes into MeCHO and *Me fumaraldehydate*, m.p. 35—36° (2 : 4-*dinitrophenylhydrazone*, m.p. 194°), yielding AcOH and $CO_2H{\cdot}CH{:}CH{\cdot}CO_2Me$. E. S. H.

Oxidation of phenols by peracetic acid. Passage from the aromatic to the aliphatic series. J. Böeseken and C. F. Metz (Rec. trav. chim., 1935, **54**, 345—352).—p-$C_6H_4Br{\cdot}OH$ with AcO_2H after 2 months gives β-*bromomuconic acid* (I), m.p. 213°, and β-*bromo-γδ-dihydroxy-γδ-dihydromuconolactone*, m.p. 167—168°. m-$C_6H_4Br{\cdot}OH$ also gives (I), but 2 : 4-$C_6H_3Br_2{\cdot}OH$ and 2 : 4 : 6-$C_6H_2Br_3{\cdot}OH$ are not oxidised. p-$C_6H_4Cl{\cdot}OH$ similarly gives β-*chloromuconic acid*, m.p. 223°, and β-*chloro-γδ-dihydroxy-γδ-dihydromuconolactone*, m.p. 177°. o-$C_6H_4Cl{\cdot}OH$ gives *α-chloromuconic acid*, m.p. 190°, and δ-*chloro*-$\Delta^{\alpha\gamma}$-*hexadienaldehydic acid*, m.p. 145°. p-Cresol gives β-*methylmuconic acid*, m.p. 188·5°, and a *lactonic acid*, $C_7H_8O_4$, m.p. 124°; the mother-liquors with HCl in MeOH yield a *Me* ester, $C_8H_{10}O_4$, b.p. 135° (high vac.). The configuration of the products is discussed. F. R. G.

Carbon dioxide cleavage from dibromomalonic acid.—See this vol., 709.

Transposition of insoluble tartrates by means of sodium carbonate solution. D. H. Hart and D. Papa (Rec. trav. chim., 1935, **54**, 358—360).—1 g. of the common insol. tartrates after boiling with 50 c.c. of 1·5*M*-Na_2CO_3 for 3 min. is 70—100% decomposed to Na tartrate. Special procedures have been devised for determining tartrate in Bi, Sn^{II}, Fe^{II}, and Ag salts. R. S. B.

Activation of *r*-tartaric acid by optically active malic acid. A. McKenzie and E. W. Christie (Biochem. Z., 1935, **277**, 122—128).—K *d*- and *l*-tartrate have the same solubility in aq. solution of *d*- or *l*-malic acid, and the optical activation obtained in crystals separating on adding *d*- or *l*-malic acid to neutralised solution of *r*-tartaric acid is not due to such differences in solubility. P. W. C.

Conversion of the salts of *iso*propylidene sugar acids into methyl esters. T. Reichstein, A. Pedolin, and A. Grüssner (Helv. Chim. Acta, 1935, **18**, 598—601).—The salt is suspended or dissolved in MeOH and treated at a very low temp. with excess of HCl–MeOH followed immediately by CH_2N_2. The

duration of dangerous acidity is thus reduced to a tolerable min. *K* dl-iso*propylideneglycerate* (I), obtained by oxidising *iso*propylideneglycerol with $KMnO_4$–KOH, thus yields *Me* dl-iso*propylideneglycerate*, b.p. 80°/11 mm., and K *d-iso*propylidenexyluronate gives the corresponding *Me* ester, b.p. 182°/13 mm., m.p. 103—104° (corr.), $[\alpha]_D^{21}$ −32·8°±0·5° in MeOH. (I) and $SOCl_2$ in Et_2O yield dl-iso*propylideneglyceryl chloride*, b.p. about 58°/12 mm. H. W.

Optical rotations and other properties of the lead and calcium aldonates. H. S. Isbell (J. Res. Nat. Bur. Stand., 1935, **14**, 305—315).—The prep. of the following substances is described: Pb gluconate, $[\alpha]_D^{20}$ −5·2°; Pb xylonate, $[\alpha]_D^{20}$ −6·8°; *Pb galactonate*, $[\alpha]_D^{20}$ −12·9°; *Pb arabonate*, $[\alpha]_D^{20}$ −6·70°; *Pb mannonate*, $[\alpha]_D^{20}$ −5·50°; *Ca xylonate*, $[\alpha]_D^{20}$ +13·5°—0·53 *c* (where *c* is the no. of g. of salt in 100 ml.); *Ca α-glucoheptonate*, $[\alpha]_D^{20}$ +5·95° in H_2O. Addition of Pb salts to the Ca salts of the α-OH-acids causes large changes in [α], which follow the configuration of the α-C atom in the aldonic acid. The Pb aldonates are acids, which can be titrated with alkali and hydrolyse in solution giving small quantities of free aldonic acids which undergo lactone formation, causing small changes in rotation. E. S. H.

Electrolytic oxidation of xylose in presence of alkaline-earth bromides and carbonates. H. S. Isbell and H. L. Frush (J. Res. Nat. Bur. Stand., 1935, **14**, 359—362).—Using graphite electrodes the reaction yields *Ca*, *Mg*, $[\alpha]_D^{20}$ +14·70° in H_2O, or Sr xylonate. E. S. H.

Errors in determination of vitamin-*C*.—See this vol., 670.

Degradation of *l-iso*propylideneascorbic acid. T. Reichstein, A. Grüssner, and W. Bosshard (Helv. Chim. Acta, 1935, **18**, 602—608).—*l-iso*Propylideneascorbic acid is oxidised by $KMnO_4$–KOH to *K* l-iso*propylidenethreonate*, m.p. 158° (corr.), $[\alpha]_D^{22}$ +24·8° in H_2O, converted by HCl–MeOH immediately followed by CH_2N_2 into *Me* l-iso*propylidenethreonate* (I), b.p. 65°/0·1 mm., 125°/12 mm., $[\alpha]_D^{21}$ +21·3° in $COMe_2$ (corresponding *amide*, m.p. 89—90°, $[\alpha]_D^{19}$ +42·9° ±3° in $COMe_2$. (I) is hydrolysed by hot H_2O to *l*-threonic acid, $[\alpha]_D^{19}$ +9·54° in H_2O [corresponding *quinine* salt, m.p. 163—165° (corr.)]. Treatment of (I) with Ag_2O and MeI in Et_2O yields *Me* l-*methyl*iso*propylidenethreonate* (II), b.p. 110°/12 mm., $[\alpha]_D^{22}$ +49·7° in MeOH, $[\alpha]_D^{21}$ +49·0° in anhyd. $COMe_2$ (corresponding *amide*, m.p. 96·5—97·5° (corr.), $[\alpha]_D^{23}$ +43·7° in $COMe_2$). Treatment of (II) with hot H_2O leads to l-*methylthreonolactone*, b.p. about 120—125°/0·3 mm. *l-Methylthreonamide*, m.p. 105—106°, $[\alpha]_D^{22}$ +96·4° in MeOH, *brucine* l-*methylthreonate* (+5H_2O), m.p. 151—153° (corr.), and *quinine* l-*methylthreonate* (+1·5H_2O), m.p. 179° (corr.), are described. H. W.

Detection and determination of gluconic acid. W. Diemair, B. Bleyer, and L. Schneider (Z. Unters. Lebensm., 1935, **69**, 212—220).—≮ 12 mg. of α-gluconic acid (I) may be detected in presence of glycerol, sorbitol, tannin, and malic and citric acids by pptn. as the phenylhydrazide (II), but the determination of (I) is inaccurate owing to adsorption of (II) by C used for purifying the aq. solution. Detection of (I) in presence of *d*-glucose (III) is difficult owing to co-pptn. of the osazone (IV) of (III), but (II) may be separated from (IV) by reason of its greater solubility in hot H_2O. (I) could not be detected in pure apple-juice or cider. E. C. S.

Preparation of 5-ketogluconic acid by bromine oxidation. E. W. Cook and R. T. Major (J. Amer. Chem. Soc., 1935, **57**, 773).—The reducing substance which remains after protracted oxidation of glucose to gluconic acid by electrolytic Br is identified as δ-ketogluconic acid. R. S. C.

Preparation of *d*-mannuronic acid and its derivatives. R. G. Ault, W. N. Haworth, and E. L. Hirst (J.C.S., 1935, 517—518).—α-Methylmannoside and dry 1% HCl–$COMe_2$ give the 2 : 3-iso*propylidene* (I), m.p. 105°, b.p. 145°/0·02 mm., $[\alpha]_D^{20}$ +28·3° in MeOH, +24·3° in H_2O, and 2 : 3-4 : 6-*di*iso*propylidene*, m.p. 76°, derivatives. The structure of (I) is proved by quant. hydrolysis by 0·01*N*-HCl at 15° to α-methylmannopyranoside. (I) and $KMnO_4$–KOH at 15—20° give *K* 2 : 3-iso*propylidenemannuronide*, amorphous, hygroscopic, $[\alpha]_{5780}^{17}$ −4·5° in H_2O, hydrolysed by 0·02*N*-HCl at 50° (1 hr.) to *K* α-*methyl*-α-*mannuronide* (II), +0·5EtOH, decomp. about 230°, $[\alpha]_{5780}^{17}$ +48° in H_2O, and amorphous, which with $HClO_4$ gives α-*methylmannuronide hydrate* (H_2O lost slowly at 80—90°/vac.), m.p. 108°, $[\alpha]_{5780}^{19}$ +65·6° in H_2O. This with 2·5% HCl at 100° yields (9 hr.) *d*-mannuronolactone, m.p. 143—144°, $[\alpha]_D^{20}$ +95° (const.) in H_2O. (II) with Me_2SO_4–KOH, followed by MeI–Ag_2O, affords the *Me* ester, b.p. 118°/0·02 mm., $[\alpha]_{5780}^{20}$ +74° in MeOH, +61·4° in $CHCl_3$, of 2 : 3 : 4-*trimethyl*-α-*mannuronide* (III), hydrolysed by boiling *N*-NaOH to (III), b.p. 156—158°/0·02 mm., $[\alpha]_{5780}^{21}$ +73° in MeOH (salts and derivatives, oils). R. S. C.

Methyl *d*-galacturonate and ascorbic acid. T. Reichstein and A. Grüssner (Helv. Chim. Acta, 1935, **18**, 608—610).—β-*d*-Galacturonic acid (I) is converted by CH_2N_2 in MeOH into *Me* α-d-*galacturonate* (II), m.p. 134—135·5° (corr.; microscope), $[\alpha]_D^{18}$ +75·8° to 44° in H_2O, $[\alpha]_D^{18}$ +39° (equilibrium val.) in MeOH. Treatment of (I) with alkali or of (II) with $Al(OPr^{\beta})_3$ affords only min. amounts of reducing substances, thus indicating the non-production of ascorbic acid. H. W.

Methylglucosides of naturally occurring hexuronic acids. IV. Polygalacturonic acid methylglucosides derived from Ehrlich's "Pektolsäure" and "Pektolactonsäure." L. Baur and K. P. Link (J. Biol. Chem., 1935, **109**, 293—299).—The view of Ehrlich (A., 1929, 1273; 1930, 1163; 1932, 1063) that pectins contain basic units, each composed of 4 galacturonic acid mols., in ring ["pektolsäure" (I)] and open-chain ["pektolactonsäure" (II)] structures, is disproved. By treating citrus and apple pectins with HCl, acids are obtained with [α] etc. agreeing with Ehrlich's vals., but treatment with HCl–MeOH (cf. A., 1933, 595) dissolves only 30% of (I) and 90% of (II), and analysis of the methylglucosides of the residual Me polygalacturonate, and of the free acid and its Na and Ba salts,

shows that the residue contains approx. 10 galacturonic acid units in the mol. (cf. A., 1934, 633). E. W. W.

Synthesis of polyketocarboxylic acids of the fatty acid series. I. E. LEHMANN and W. GRABOW (Ber., 1935, 68, [*B*], 703—707).—Addition of $COMe_2$ and $Et_2C_2O_4$ to Na wire under Et_2O and decomp. of the product with a large excess of acid gives *Et* αγεζθ-*pentaketodecoate* (I), m.p. 144° (also $+1H_2O$, m.p. 119°), which gives a blackish-brown colour with $FeCl_3$ and is readily decomposed by alkali or alkali carbonates. When heated with $ZnCl_2$ at 145° (I) passes into *Et H chelidonate*, m.p. 227° (whence chelidonic acid, m.p. 262°), and *Et* 6-α*γ-diketobutyl*-4-*pyrone*-2-*carboxylate* (II), pale yellow needles or cubes, m.p. 99°, hydrolysed by NaOH to $H_2C_2O_4$ and small amounts of an isomeric *ester*, m.p. 57°. Very cautious treatment of (II) with Na_2CO_3 leads to 6-α*γ-diketobutyl*-4-*pyrone*-2-*carboxylic acid* (III), m.p. 213° (*Me* ester, needles or granules, m.p. 124°). With Br in $CHCl_3$ (II) affords *Et* 6-β-*bromo*-α*γ-diketobutyl*-4-*pyrone*-2-*carboxylate*, m.p. 140°. Treatment of (III) with boiling 20% HCl gives αγεζθ-*pentaketodecoic acid*, m.p. 204° (decomp.), re-converted by MeOH–HCl into (III), and αγεζ-*tetraketo-octoic acid*, m.p. 210° (decomp.). H. W.

Action of methyl chlorosulphonate on methyl acetate; action of methyl sulphate on acetyl chloride. R. LEVAILLANT (Compt. rend., 1935, 200, 1053—1055).—$ClSO_3Me$ (1 mol.) containing $ZnCl_2$ at 140—160° with MeOAc (> 1 mol.) gives *Me* α-*methylsulphoacetate*, b.p. 157°/21—22 mm., also formed from AcCl with Me_2SO_4 containing $ZnCl_2$ at 140—150°. J. L. D.

Photosynthesis of formaldehyde in tropical sunlight.—See this vol., 713.

Catalytic decomposition of acetaldehyde.—See this vol., 711.

Thermal decomposition of acetaldehyde and propaldehyde.—See this vol., 708.

Catalytic action of monoses on the formaldehyde condensation. A. KUSIN (Ber., 1935, 68, [*B*], 619—624).—Complete condensation of 4% CH_2O at 35—40° is caused by Ca fructosate (I) in 1—3 hr., whereas under the same conditions an equiv. amount of $Ca(OH)_2$ has no appreciable effect in 5 hr. An analogous acceleration is caused by fructose (II) and $Ca(OH)_2$ or $Pb(OH)_2$. Since glycerol and mannitol are inactive the effect cannot be due to the polyhydroxy-groups. The absence of acceleration by sucrose (III) and the catalytic activity of glycollaldehyde (IV) exclude the possibility that cyclic forms (amylene- or butylene-oxide) or a semi-acetal OH participate in the change. The approx. equal catalytic activity of (II), glucose, maltose, and (III) does not justify the assumption that activity is due to free CO or CHO, but strongly suggests that the enol grouping with 2OH is responsible for the change. Catalytic activity is not observed when the formation of an enol [fructose penta-acetate or (III)] is rendered difficult. Condensation of CH_2O in presence of (II) does not take place at $p_H < 12$. Change occurs slowly at p_H 12; at p_H 12·6 acceleration is similar to that observed with $Pb(OH)_2$ and at p_H 14·9 analogous to that produced by $Ca(OH)_2$. The enhancement of the solubility of (I) in 50% MeOH at 0° by CH_2O indicates the production of unstable, intermediate products apparently derived mainly from unimol. CH_2O; this view is supported by observations of the f.p. of solutions of (I) and CH_2O, separately and when mixed. It is suggested that a monose in active enol form accelerates the conversion of CH_2O into sugars in the green parts of plants. H. W.

Highly sensitive reaction for the characterisation and determination of citral. J. BOUGAULT and E. CATTELAIN (J. Pharm. Chim., 1935, [viii], 21, 437—449).—The colour of methylene-blue in NaOH–MeOH slowly changes from blue to pink. The change is faster at 23° than at 0°, and in 0·1*N*- than in 0·01*N*-NaOH. It is greatly catalysed by citral (0·02 mg. in 5 c.c.), which may be determined colorimetrically by this effect. Many other substances have a similar action, but only in much larger quantities (74—867 mg.). R. S. C.

Glyoxal. II. Glyoxal semiacetal. H. O. L. FISCHER and E. BAER (Helv. Chim. Acta, 1935, 18, 514—521; cf. A., 1926, 599).—Attempts to obtain *glyoxal* Et_2 *acetal* (I) by treatment of $CH_2{:}CH{\cdot}CH(OEt)_2$ with dil. O_3 in EtOAc at low temp. and reduction of the ozonide (Pd–$BaCO_3$) were unsuccessful. Interaction of glyceraldehyde Et_2 acetal (improved prep.) with $Pb(OAc)_4$ in C_6H_6 affords (I), b.p. 42—43°/12—13 mm., in 53·7% yield. (I) slowly polymerises when preserved, but the product becomes spontaneously depolymerised in solution or when distilled in vac. (I) is transformed by $NHPh{\cdot}NH_2$ in dil. AcOH at 100° into glyoxaldiphenylhydrazone, m.p. 171—172°, and by $CH(OEt)_3$ and NH_4Cl in EtOH into glyoxal Et_4 acetal, b.p. 81—83°/10 mm. (I) is slowly converted by cold *N*-KOH into glycollaldehyde Et_2 acetal and $CH(OEt)_2{\cdot}CO_2H$.

[With H. NIDECKER.] The action of MgMeI in Et_2O on (I) gives *lactaldehyde* Et_2 *acetal* (II), b.p. 63—64°/12 mm., hydrolysed to lactaldehyde (III), m.p. 105—106°. Treatment of (II) with p-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$ in the requisite proportion gives the *p*-nitrophenylhydrazone, m.p. 127—128°, and *p*-nitrophenylosazone, decomp. 306—309°, of (III). H. W.

Fluorination of organic compounds. I. P. C. RÂY, H. C. GOSWAMI, and A. C. RAY (J. Indian Chem. Soc., 1935, 12, 93—95).—When heated with anhyd. TlF at 85—95°, CH_2AcBr, CH_2BzBr, and $CH_2Br{\cdot}CH(OEt)_2$ afford, respectively, *fluoroacetone*, b.p. 72·5° [*semicarbazone*, m.p. 131·5° (decomp.)], ω-*fluoroacetophenone*, b.p. 98°/18 mm. (*pyridinium*, m.p. 161° and *quinolinium*, darkens 231°, salts), and *fluoroacetal*, b.p. 60°/25 mm. J. W. B.

Hydroxymethylene ketones and their reaction products. V. Hydrolytic fission of double linkings conjugated with the carbonyl group. VI. Proof of αδ-addition of Grignard salts to the conjugated double linkings of hydroxymethylene ketones. R. E. MEYER (Helv. Chim. Acta, 1935, 18, 461—466; 467—470; cf. this vol., 609).—V. β-Methyl-$\Delta^{\beta\eta}$-nonadien-ζ-one is converted by prolonged boiling with aq. K_2CO_3 into methylheptenone

and MeCHO. Similar results are recorded with β-methyl-Δ$^{\eta}$-nonen-ζ-one and θμ-dimethyl-Δ$^{\beta\eta\lambda}$-tridicatrien-δ-one. These observations and evidence from the lit. lead to the rule that double linkings conjugated with CO can be hydrolysed by alkali; H is added to the fragment carrying CO, whilst the original β-C forms a new CO.

VI. The action of MgEtI on the Mg salt of hydroxymethylenemethylheptanone gives OH·CO-compounds which on subsequent fission afford only methylheptanone and no trace of a higher ketone. Products, OH·CREt·CH_2·CHO, are therefore not formed. Addition of MgMeI or MgEtI to OH·CH compounds of Me ketones occurs exclusively in the αδ-position and CO is not attacked. The synthesis of αβ-unsaturated aldehydes cannot therefore be effected along these lines, but a method is afforded of introducing the group :CHR into ketones even when the latter do not condense with aldehydes. *β-Methyl-Δ$^{\eta}$-decen-ζ-one*, b.p. 104—105°/12 mm., is described. H. W.

"Ketol," OH·CHAc·CH_2Ac. M. Henze (Z. physiol. Chem., 1935, **232**, 123—124).—The liquid ketol (I), b.p. 113·5/12 mm., on keeping gives a cryst. *modification* (II), m.p. in glass 95°, in Jena glass 124—128°, in quartz 130—132°. (II) is a dimeric form; the *Me ether* of (I), m.p. 162°, is also dimeric. J. H. B.

Rapid method for determination of reducing sugars. G. A. Bravo (Boll. Uff. Staz. Sperim. Ind. Pelli, 1935, **13**, 81—91).—The solution containing the sugar (in small quantity) is treated with a given quantity (excess) of Fehling's solution, accurately prepared, and the filtrate examined colorimetrically. From the colorimeter reading, the sugar content is read off on an empirical scale. E. W. W.

Preparation of *l*-xylose. H. Appel (J.C.S., 1935, 425—426; cf. Vargha, this vol., 325).—Triethylidenesorbitol (cf. Helferich and Appel, A., 1931, 1038) heated with 50% aq. AcOH gives 1 : 2 : 3 : 4-*diethylidenesorbitol*, m.p. 212—214°, $[\alpha]_D^{17}$ −11·1° in H_2O, which with $Pb(OAc)_4$ in C_6H_6 and AcOH and subsequent hydrolysis with 2*N*-H_2SO_4 gives *l*-xylose. F. R. G.

***d*-Talose, diacetone (di*iso*propylidene-)*d*-talose, and diacetone (di*iso*propylidene-)*d*-talonolactone.** W. Bosshard (Helv. Chim. Acta, 1935, **18**, 482—490).—*d*-Galactonolactone is partly epimerised by C_5H_5N–H_2O at 130—135° and, after removal of *d*-galactonic acid as the Cd salt, *d*-talonic acid is isolated as the *K* salt, m.p. 171—172°, $[\alpha]_D^{10}$ +2·97° in H_2O. Reduction of *d*-talonolactone (I) by Na–Hg in H_2O leads to *d*-talose (II), m.p. 128—130° (Reichert microscope), $[\alpha]_D^{21}$ about +30° to $[\alpha]_D^{21}$ +20·6° in H_2O. Isolation of (II) from the crude syrup can also be effected through its *o-nitrophenylhydrazone*, m.p. 148·5—149°, $[\alpha]_D^{18}$ +88·3° in MeOH; indications of the formation of β-talose, m.p. 123—127°, are obtained. Treatment of (I) with $COMe_2$ containing $CuSO_4$ and a little conc. H_2SO_4 leads to a non-cryst. mixture (III) consisting mainly of 1 : 2·5 : 6-*di*iso*propylidenetalofuranose*, b.p. 110—120°/0·5 mm., $[\alpha]_D^{20}$ −25·2° in $COMe_2$, which does not reduce I solution. Oxidation of (III) with $KMnO_4$ gives very small amounts of αβδε-di*iso*propylidenetalonic acid, isolated as the corresponding *lactone*, m.p. 129—130°, $[\alpha]_D^{21}$ +17°±2° in $COMe_2$ [also obtained from (I) and $COMe_2$–$CuSO_4$–H_2SO_4]. (III) therefore contains 2 : 3·5 : 6-di*iso*propylidenetalofuranose. H. W.

***d*-Gulomethylose (6-deoxy-*d*-gulose) and its relation to a reported inversion of *l*-rhamnose.** P. A. Levene and J. Compton (J. Amer. Chem. Soc., 1935, **57**, 777—778).—By the cyanohydrin reaction, followed by reduction with Na–Hg, 5-deoxy-*d*-xylose affords d-*gulomethylonic* (6-*deoxy*-d-*gulonic*) *acid*, $[\alpha]_D$ −5·0° in H_2O (*Na* salt, $[\alpha]_D$ +11·03° in H_2O), and *lactone*, m.p. 180—181°, $[\alpha]_D$ −68° in H_2O (p-*bromophenylhydrazide*, m.p. 132—133°, $[\alpha]_D$ +8·83° in H_2O), and d-*gulomethylose* (6-*deoxy*-d-*gulose*), amorphous, $[\alpha]_D$ −35·7° (const.) in H_2O [p-*bromophenyl-hydrazone*, m.p. 135°, $[\alpha]_D$ −16·1° ⟶ +9·2° in EtOH, and *-osazone*, m.p. 195—196°, $[\alpha]_D$ 0° ⟶ 15·3° in C_5H_5N–EtOH (3 : 2)], thus disproving the inversion postulated by Muskat (this vol., 199), which is also not in line with hydrolysis of di*iso*propylideneglucose and 5-methyl*iso*propylidenexylose 3-*p*-toluenesulphonates. R. S. C.

6-Deoxy-*d*-gulose. I. E. Muskat (J. Amer. Chem. Soc., 1935, **57**, 778).—The substances of Levene *et al.* (preceding abstract) may not have the structures claimed. R. S. C.

Action of phosphate on hexoses. I. Formation of acetol from glucose in acid solutions of potassium phosphate. R. Nodzu (Bull. Chem. Soc. Japan, 1935, **10**, 122—130).—Glucose (I) on prolonged boiling with 40% KH_2PO_4–K_2HPO_4 at p_H 4·8—7·1 affords a distillate which contains AcCHO (II), Ac_2, and CH_2Ac·OH (III) (cf. A., 1905, i, 3) isolated as their semicarbazones. 4—5% of (I) is converted into (III), which is determined in the distillate by Fischler's method (A., 1928, 870). The initial p_H influences only the rate of formation (max. at p_H 7·0—7·1) of (III). (I) as above with 5% of the phosphate mixture gives a low yield of (III) and a slower rate of formation. J. L. D.

Composition of altered glucose solutions. N. Mayer (Compt. rend., 1935, **200**, 1116—1118).—Glucose (2%) in 0·1*N*-NaOH after 30 min. at 100° in vac. loses its rotatory power and the solution contains HCO_2H, AcOH, and lactic acid in addition to substances capable of reducing methylene-blue. Traces of redoxin (?) and AcCHO have been found. F. N. W.

Partition of tri- and tetra-methylglucoses between chloroform and water.—See this vol., 695.

Tritylation of sugar mercaptals. M. L. Wolfram, J. L. Quinn, and C. C. Christman (J. Amer. Chem. Soc., 1935, **57**, 713—717).—Glucose Et mercaptal, when treated with CPh_3Cl in C_5H_5N and then with BzCl, gives d-*glucose Et mercaptal* 2 : 3 : 4 : 5-*tetrabenzoate* 6-*CPh$_3$ ether*, m.p. 161—162°, $[\alpha]_D^{21}$ +49° in $CHCl_3$, which with dry HBr–$CHCl_3$ gives *d*-glucose Et mercaptal 2 : 3 : 4 : 5-tetrabenzoate 6-bromide, m.p. 169—170°, $[\alpha]_D^{24}$ +39° in $CHCl_3$. This with NaI–$COMe_2$ at 115° gives the 6-*iodide*, m.p. 165—166°, $[\alpha]_D^{25}$ +39°, hydrolysed by $AgNO_2$ in hot $COMe_2$, followed by $CaCO_3$ and $HgCl_2$, to *d*-glucose 2 : 3 : 4 : 5-

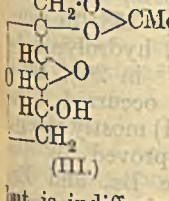
tetrabenzoate, m.p. 118—119°, $[\alpha]_D^{25}$ +69° in EtOH. Galactose affords similarly d-*galactose Et mercaptal* 2 : 3 : 4 : 5-*tetrabenzoate* 6-*CPh*$_3$ *ether*, m.p. 138—139°, $[\alpha]_D^{30}$ −22·5° in $CHCl_3$, or by AcCl the corresponding *tetra-acetate* (I), m.p. 123—124°, $[\alpha]_D^{21}$ −22·5° in $CHCl_3$. Arabinose and xylose give l-*arabinose*, m.p. 101—102°, $[\alpha]_D^{27}$ −24° in $CHCl_3$, and d-*xylose Et mercaptal* 2 : 3 : 4 : 5-*tetra-acetate* 6-*CPh*$_3$ *ether*, m.p. 149—150°, $[\alpha]_D^{21}$ −20·5° in $CHCl_3$. (I) and HBr–AcOH gives d-*galactose Et mercaptal* 2 : 3 : 4 : 5-*tetra-acetate* (II), m.p. 96—97°, $[\alpha]_D$ −6·8° in $CHCl_3$, or occasionally its 6-*bromide*, m.p. 110—111°. Hydrolysis ($CdCO_3$–$HgCl_2$) of (II) gives *d*-galactose 2 : 3 : 4 : 5-tetra-acetate hydrate, m.p. 162°, $[\alpha]_D^{25}$ +10° ⟶ −38° in C_5H_5N, whereas (I) gives similarly the *semiacetal*, m.p. 153°, $[\alpha]_D^{25}$ −28° (stable) in $CHCl_3$, −29·5° ⟶ −16·5° in MeOH, of aldehydo-d-*galactose* 2 : 3 : 4 : 5-*tetra-acetate* 6-*CPh*$_3$ *ether* (*semicarbazone*, m.p. variable, $[\alpha]_D^{27}$ +200° in $CHCl_3$).

R. S. C.

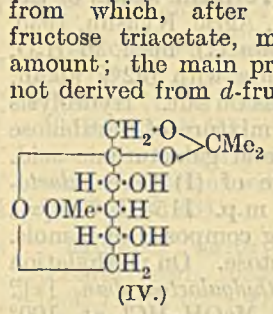
Ketone sugar series. IV. Preparation of methyl- and ethyl-fructoside acetates. E. Pacsu (J. Amer. Chem. Soc., 1935, 57, 745—747; cf. A., 1933, 937).—β-Acetochlorofructopyranose (I) and $AgNO_3$ in MeOH (*a*) with or (*b*) without C_5H_5N give β-fructose tetra-acetate (II) (2%), Schlubach's (? α-) methylfructoside tetra-acetate [(*a*) 18, (*b*) 34%] (A., 1928, 873), and β-*methylfructose*<2 : 6> *tetra-*(*ortho-*)*acetate*, a glass, $[\alpha]_D^{20}$ −13·6° in $CHCl_3$ [(*a*) 80, (*b*) 64%], which with alkali gives β-*methylfructoside* 3-(*ortho-*)*acetate*, cryst., $[\alpha]_D^{20}$ −12·4° in H_2O, and with dil. acid, aq. MeOH, or hot H_2O gives (II). (I) and Ag_2O in EtOH give (II), a β-*ethylfructoside tetra-acetate*, m.p. 103—104°, $[\alpha]_D^{20}$ +51·6° in $CHCl_3$, and β-*ethylfructoside tetra-*(*ortho-*)*acetate*.

R. S. C.

Acetone [*iso*propylidene] compounds of sugars and their derivatives. XIX. Transition, *d*-fructose ⟶ *d*-psicose (ψ-fructose) ⟶ *d*-sorbose. H. Ohle and F. Just (Ber., 1935, 68, [*B*], 601—609; cf. A., 1933, 492).—Hydrolysis of α-di*iso*propylidenefructose *p*-toluenesulphonate (I) with 80% AcOH at 60° leads to 1 : 2-iso*propylidene*-α-*fructose* 3-p-*toluenesulphonate* (II), m.p. 124·5° (subsequent decomp.), $[\alpha]_D^{20}$ −113·0° in $CHCl_3$, which regenerates (I) with $COMe_2$ and $CuSO_4$. (II) or *iso*propylidene-α-fructose and *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_5H_5N at 40° give *isopropylidene*-α-*fructose tri*-p-*toluenesulphonate*, m.p. 125·5°, $[\alpha]_D^{20}$ −121·4° in $CHCl_3$. iso*Propylidene*-α-*fructose* 4 : 5-*diacetate* 3-p-*toluenesulphonate*, m.p. 97°, $[\alpha]_D^{20}$ −133·0° in $CHCl_3$ [from (II) and Ac_2O in C_5H_5N], and iso*propylidene*-α-*fructose* 4 : 5-*dibenzoate* 3-p-*toluenesulphonate*, m.p. 144°, $[\alpha]_D^{20}$ −316·2° in $CHCl_3$, are described.


(III.)

Treatment of (II) with *N*-NaOH in EtOH at 100° leads to 1 : 2-iso*propylidene* - 3 : 4 - *anhydro*-d-*psicose* (III) (psicose = ψ-fructose), m.p. 80°, $[\alpha]_D^{20}$ −47·6° in $CHCl_3$, which reduces boiling Fehling's solution, but is indifferent towards cold OI'. The ethyleneoxide ring is sufficiently stable to allow (III) to be transformed by Ac_2O in C_5H_5N at 20° or by a large excess of boiling Ac_2O into 1 : 2-iso*propylidene*-3 : 4-*anhydro*-d-*psicose* 5-*acetate*, m.p. 81°, $[\alpha]_D^{20}$ +5·9° in $CHCl_3$, by BzCl in C_5H_5N at 40° into the corresponding 5-*benzoate*, m.p. 111·5°, $[\alpha]_D^{20}$ +24° in $CHCl_3$, and into the 5-p-*toluenesulphonate*, m.p. 95°, $[\alpha]_D^{20}$ +4·7° in $CHCl_3$. Ag_2O and boiling MeI transform (III) into 5-*methyl*-1 : 2-iso*propylidene*-3 : 4-*anhydro*-d-*psicose*, b.p. 90—92°/0·01 mm., $[\alpha]_D^{26}$ −2·8° in $CHCl_3$. Treatment of (III) with 2*N*-NaOH at 38° gives a dark oil from which, after acetylation, *iso*propylidene-α-fructose triacetate, m.p. 97°, is isolated in small amount; the main products of fission by alkali are not derived from *d*-fructose. Addition of NaOMe in boiling MeOH to (III) leads to 4-*methyl*-1 : 2-iso*propylidene*-d-*sorbose* (IV), m.p. 112—113°, $[\alpha]_D^{20}$ −81·6° in $CHCl_3$ (3 : 5-*diacetate*, m.p. 75°, $[\alpha]_D^{16}$ −92·8° in $CHCl_3$), hydrolysed by 0·2*N*-H_2SO_4 at 100° to 4-*methyl*-d-*sorbose*, m.p. 126—127°, $[\alpha]_D^{20}$ +33·2° to +27·5° in EtOH (*phenylosazone*, m.p. 131—132°). Complete methylation of (IV) could not be effected by Ag_2O and MeI, whereas the action of MeI on the Na compound leads to 3 : 4 : 5-*trimethyl*-1 : 2-iso*propylidene*-d-*sorbose* (V), b.p. 105—106°/0·25 mm., $[\alpha]_D^{20}$ −59·6° in H_2O (3 : 4 : 5-*trimethyl*-1 : 3-iso*propylidene*-α-*fructose*, b.p. 110—111°/0·08 mm., $[\alpha]_D^{20}$ −158·7° in H_2O, is analogously obtained). Hydrolysis of (V) followed by oxidation with HNO_3 and treatment of the product with CH_2N_2 leads to $Me_2C_2O_4$, Me_2 *l*-dimethoxysuccinate (*l*-dimethoxysuccindimethylamide, m.p. 202—203°, $[\alpha]_D^{20}$ −128·9° in H_2O), and Me_2 xylotrimethoxyglutarate (xylotrimethoxyglutardimethylamide, m.p. 164·5—165°, $[\alpha]_D^{20}$ ±0°).

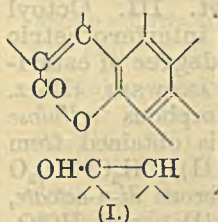

(IV.)

H. W.

Action of air on solutions of pure sucrose. M. Garino, M. Parodi, and V. Vignolo (Gazzetta, 1935, 65, 132—143).—A 20% aq. solution of sucrose is oxidised by air very slowly at 20°, more rapidly at 100°, with evolution of CO_2. At 100—130° the solution becomes brown, and glucosone and pentoses are formed. In presence of $Ca(OH)_2$, oxidation is more rapid; CO is formed, with Ca salts and volatile aldehydes.

E. W. W.

Scilla and digitalis glucosides. A. Stoll (Pharm. Acta Helv., 1934, 9, 145—168; Chem. Zentr., 1934, ii, 3625).—Partly a summary of work already reported (cf. A., 1934, 1206). The ultra-violet absorption spectra of scillaridin-*A* (I) and scillarin-*A* show similar maxima to that of octatrienoic acid; partly on this basis the partial formula (I) is proposed. Irradiation of *Scilla* products gives rise to no vitamin-*D* activity. Purpureaglucoside-*A* and deacetyldigilanide-*A* are identical. The enzymes of *Digitalis* leaves are discussed.


(I.)

H. N. R.

Thevetin, the crystalline glucoside of *Thevetia Neriifolia*. N. Ghatak (Proc. Acad. Sci., U.P., India, 1934, 4, 173—174).—A criticism of Chen *et al.* (A., 1934, 820). Thevetin is $C_{20}H_{30}O_6$ and is hydrolysed to glucose and *thevetigenin*, $C_{14}H_{20}O$, a OH-compound which gives an *Ac* derivative.

H. G. M.

Solanine. A. Heiduschka and F. Philippi (Ber., 1935, 68, [*B*], 669).—Acetylation of solanine according to Zemplén *et al.* (A., 1929, 51) affords *solanine hendeca-acetate*, $C_{74}H_{113}O_{29}N$, m.p. 200° after darkening at 182° and softening at 192°, hydrolysed by boiling 12% HCl to solanidine hydrochloride. H. W.

Galactoaraban prepared from the seeds of the peanut. R. Miyama (J. Dept. Agric. Kyushu, 1935, 4, 195—236).—The *galactoaraban* (I), insol. in H_2O, was extracted from the peanuts with 0·2% alkali, pptd. with EtOH, and purified as Cu salt. Hydrolysis of (I) with 3% H_2SO_4 gave a mixture of *l*-arabinose (2 mols.), galactose (1 mol.), and galacturonic acid. Acetolysis of the hepta-acetate of (I) gave *galacto-arabotriose* (II) *nona-acetate*, m.p. 115—118°, $[\alpha]_D$ +95·4°, the trisaccharide being composed of 2 mols. of arabinose and 1 mol. of galactose. On methylation (Me_2SO_4) (I) formed *heptamethylgalactoaraban*, $[\alpha]_D^{23}$ +579·9°, hydrolysed by 1% MeOH–HCl at 100° to a mixture from which 2 : 3 : 4-trimethylgalactose and 2 : 3-dimethyl-*l*-arabinose were isolated. (I) is considered to be composed of polymerised (II), the individual sugar units being linked together through the 1 and 4 positions. M. S.

Xanthate formation of some polymeric carbohydrates. T. Lieser and A. Hackl (Technol. u. Chem. Papier- u. Zellstoff-Fabr., 1934, **31**, 69—73; Chem Zentr., 1934, ii, 3926).—Optimal conditions have been determined for xanthate formation from starch, glycogen (I), lichenin, mannan, inulin, and xylan. The [NaOH] necessary is < with cellulose. Xanthate formation rises with increasing [NaOH] to an optimum and then decreases [with the exception of (I)]. With the exception of (I) the optimum ratio of reactants is $2C_6H_{10}O_5 : CS_2$. It is concluded that, except for (I), the same no. of sugar-anhydride chains lie in the surface as in the interior of the micelles. H. N. R.

Concentration and ionising tendency of carboxylic acid groups in cellulose and other natural products. S. M. Neale (Nature, 1935, **135**, 583).—The addition of NaCl to oxycellulose (I) liberates its acidic H ion. With excess of NaCl (I) can be titrated directly with NaOH using an indicator turning slightly on the acid side of the neutral point. L. S. T.

Compounds of high mol. wt. III. Octoyl esters of cellulose, and the interferometric method of determination of the degree of esterification of cellulose. A. Nowakowski (Rocz. Chem., 1935, **15**, 69—80).—Amorphous *cellulose tri-n-octoate* (I), m.p. 167—170°, is obtained from ramie cellulose (II), *n*-C_7H_{15}·CO_2H (III), $(CH_2Cl·CO)_2O$ (IV), and H_2SO_4 (0·1%) at 40°, fibrous *di-n-octoate*, m.p. 216—219°, from (II), (III), (IV), and $HClO_4$ (0·06%) in Et_2O at 60°, and fibrous (I), m.p. 182—186°, by soaking (II) in C_5H_5N for 5 days, adding *n*-C_7H_{15}·COCl and C_6H_6, and boiling for 42 hr. *X*-Ray examination shows that the products containing > 60% of (III) retain the structure of (II), that of (I) being found when 60—80% of (III) is present. R. T.

Bouveault's method for the preparation of aldehydes from organo-magnesium compounds and *N*-disubstituted formamides. N. Maxim and R. Mavrodineanu (Bull. Soc. chim., 1935, [v], 2, 591—600).—With 1 mol. of MgR′X, HCO·NR_2 affords mainly the aldehyde R′·CHO (Bouveault, A., 1904, i, 13), especially with formanilides, and when R′ contains a large no. of C atoms. With 3 mols. of MgR′X the main product is the *tert.*-amine: HCO·NR_2 + 2MgR′X ⟶ NR_2·CHR + MgO + MgX_2, especially when R_2=Et_2 or piperidyl, and thus are obtained: *δ-diethylamino*-n-*heptane*, b.p. 86°/20 mm. (*picrate*, m.p. 85°; *hydroferrocyanide*); *γ-ethylanilino*-, b.p. 125°/15 mm. (*picrate*, m.p. 82°; *hydroferrocyanide*), and *γ-methylanilino*-n-*pentane*, b.p. 128°/12 mm. (hydroferrocyanide); *δ-ethylanilino*-, b.p. 142°/18 mm. (*hydroferrocyanide*), *δ-methylanilino*-, b.p. 152°/18 mm. (*hydroferrocyanide*), and *δ-diphenylamino*-βζ-*dimethyl*-n-*heptane*, b.p. 185°/7 mm.; and *γ-piperidino*-n-*heptane*, b.p. 185° (*picrate*, m.p. 107°). J. W. B.

Stereochemical relationships of some optically active amines and amino-acids. I. Configuration of valine. F. Barrow and G. W. Ferguson (J.C.S., 1935, 410—418).—If *Cabcx* and *Cabcy* have the same stereochemical configuration, replacement of *c* by *y* and *x*, respectively, gives compounds, *Cabxy*, of opposite configurations, provided that the possibility of Walden inversion is avoided by making the changes such that the C–*c* linking is not affected. By this method naturally occurring valine (I) is shown to have the same configuration as *L*(+)-alanine (II), in agreement with the less trustworthy methods of optical displacement. (I) is termed *L*(+)-valine. Et α-acetamido*iso*valerate (modified prep.), b.p. 157—158°/21 mm., with Na–BuOH gives *dl*-valinol (III) [hydrochloride, m.p. 118—119° (lit. 114°); N-*Bz*, m.p. 81—82°, ON-Bz_2, m.p. 114°, and Bz_3, m.p. 135°, derivatives], also obtained (90% yield) from NO_2·$CHPr^s$·CH_2·OH and Fe–HCl–EtOH. (II) and HBr–AcOH at 130—140° give *α-bromomethyl-isobutylamine hydrobromide*, m.p. 211—212° (decomp. 203°), which is hydrogenated (Pd–C) in dil. AcOH to α-methyl*iso*butylamine (IV) (hydrochloride, m.p. 203°; p-NO_2·C_6H_4·*CO* derivative, m.p. 115°), also obtained from $CMePr^s$:NOH, b.p. 158—160°, by Na and C_5H_{11}·OH. (I) and *d*-tartaric acid in EtOH give D(−)- (V) and L(+)-*valinol* (VI) [*H* (+)-*tartrate* of (V), +H_2O, m.p. 116°, $[\alpha]_{5461}^{20}$ +102° in H_2O; *hydrochlorides*, m.p. 113° and 112—114°, $[\alpha]_{5461}^{20}$ −16·5°, +16·4° in H_2O, respectively; Bz_2, m.p. 117°, $[\alpha]_{5461}^{20}$ +20·2°, −20·1°, and Bz_3 derivatives, m.p. 119°, $[\alpha]_{5461}^{20}$ −133·8°, +133·1°, in C_5H_5N, respectively]. *L*(−)-Formylvaline, $[\alpha]_{5461}^{20}$ −19·9° in H_2O, with HCl–EtOH, followed by Ac_2O–NaOAc, affords *Et* L(−)-*α-acetamidoisovalerate* (VII), b.p. 158°/21 mm., cryst., $[\alpha]_{5461}^{15}$ −20·1° (homogeneous), hydrolysed by hot 12% HBr to (I), $[\alpha]_{5461}^{21}$ +32·77° in 20% HCl; only slight racemisation had thus occurred. Reduction (Na–EtOH) of (VII) gives (VI) mostly racemised, the identity of which was proved by the characteristic inversion of α of the Bz_2 and Bz_3 derivatives and by isolation of a little nearly pure (VI). (V) and (VI) afford the (−)- and (+)-*isomerides* (VIII) of (IV) (*hydrochloride*, m.p. 205° after sintering at 192°, $[\alpha]_{5461}^{21,15}$ −3·4°, +3·5° in H_2O, respectively; p-NO_2·C_6H_4·*CO* derivatives, m.p. 112·5, $[\alpha]_{5461}^{15,15}$

±55·8° in C_5H_5N). The Et ester hydrochloride of (II), $[\alpha]^{20}_{5461}$ +11·1° in H_2O, with MgMeI in Et_2O gives (+)-β-*hydroxy*-α-*methyl*iso*butylamine* (IX) (*hydrochloride*, m.p. 136°, $[\alpha]^{21}_{5461}$ +5·6° in H_2O; N-*Bz* derivative, m.p. 116°, $[\alpha]^{20}_{5461}$ −17·2° in C_5H_5N, +8·1° in EtOH). *dl*-(II) affords the dl-*isomeride* (X) of (IX) [*hydrochloride*, +H_2O, m.p. (anhyd.) 117°; N-*Bz* derivative (XI), m.p. 96°], which is decomposed by HBr, but with PCl_5–$CHCl_3$ gives the chloride, hydrogenated (Pd–C) in MeOH to (IV). (X) affords (IX) and its (−)-*isomeride* [(+)-*tartrate*, +H_2O, m.p. (anhyd.) 166—167° (sinters at 161°) and (nearly pure) 122° (decomp.), $[\alpha]^{18.16}_{5461}$ +22·2°, +15·6° in H_2O, respectively; *hydrochloride*, m.p. 140°, $[\alpha]^{19.20}_{5461}$ +6·1, −5·5° in H_2O; *Bz* derivative, m.p. 116·5°, $[\alpha]^{21}_{5461}$ −16·8°, +17·7° in C_5H_5N, $[\alpha]^{21.19}_{5461}$ +8·3°, −8·0° in EtOH, respectively], which yield by PCl_5 a mixture of NH_2·CHMe·CMe_2Cl and NH_2·CHMe·CMe:CH_2, hydrogenated to (VIII) (hydrochloride, $[\alpha]^{20}_{5461}$ −2·1°, +2·4° in H_2O; *p*-NO_2·C_6H_4·CO derivative, $[\alpha]^{17}_{5461}$ +53·8°, −43·5° in C_5H_5N). *dl*-Benzoylalanine Me ester hydrochloride (modified prep.), m.p. 81°, with MgMeI gives an 80% yield of (XI), which could not be converted into the *N*-benzoyl-α-methyl*iso*butylamine and was largely decomposed by hot KOH–EtOH. R. S. C.

Complex salts of amino-acids and peptides. I. Metal complex salts of glycine and their specificity. M. Bergmann and S. W. Fox (J. Biol. Chem., 1935, **109**, 317—324).—The trioxalato-complex appears to be a sp. reagent for glycine (I), the nature of the central metal atom being of secondary importance. The presence of another cation (K, possibly NH_4 but not Na) is necessary for formation of a ppt. A method of separating (I) from gelatin hydrolysates is thus afforded. The following *salts* are described:

[R=(I)]: $[Cr(C_2O_4)_3]_4K_2$,2HCl,22H_2O;
$[Cr(C_2O_4)_3]_9K_{18}R_9$,HCl; $[Cr(C_2O_4)_3]_6K_{13}R_5$,2$H_2O$ (also 3H_2O); $[Co(C_2O_4)_3]_9K_{18}R_9$,HCl(?);
$[Co(C_2O_4)_3]_2K_4R_2$,HCl(?); $[Co(C_2O_4)_3]_4K_{11}R$,14H_2O;
$[Fe(C_2O_4)_3]_6K_{12}R_6$,HCl,$H_2O$(?);
$[Fe(C_2O_4)_3]_6K_{13}R_5$,HCl,4$H_2O$;
$[Fe(C_2O_4)_3]_2K_4R_2$,HCl. H. T.

Action of iodoethyl alcohol on thiol compounds and proteins. D. R. Goddard and M. P. Schubert (Biochem. J., 1935, **29**, 1009—1011).—CH_2I·CH_2·OH (I) with cysteine gives *S*-(β-hydroxyethyl)cysteine. The reaction of (I) with glutathione and reduced wool protein (A., 1934, 1238) at p_H 7·5 as followed by reduction in the I titre is similar to that of CH_2I·CO_2H, but slower. H. D.

Preparation of the optically active isomerides of homocystine and demonstration of their configurative relationship to naturally occurring methionine. V. du Vigneaud and W. I. Patterson (J. Biol. Chem., 1935, **109**, 97—103).—Homocystine (A., 1933, 151) is reduced by Na in liquid NH_3, and treated with CH_2PhCl, and the resulting *dl-S*-benzylhomocysteine [new m.p. 240—250° (corr.)] converted by HCO_2H in Ac_2O into *N-formyl*-dl-S-*benzylhomocysteine*, m.p. 85—86° (corr.). This yields the *brucine* salt, m.p. 125—128°, $[\alpha]^{26}_D$ −17°, of *N-formyl*-d-S-*benzylhomocysteine*, m.p. 247—252°, $[\alpha]^{26}_D$ −25° in *N*-HCl, which when treated with Na in NH_3 and with air in presence of $FeCl_3$ gives d-*homocystine* (I), m.p. 281—284° (corr.), $[\alpha]^{26}_D$ −77° in *N*-HCl, $[\alpha]^{21}_D$ +16° in H_2O. The mother-liquors similarly treated yield l-*homocystine* (II), $[\alpha]^{26}_D$ +77° in *N*-HCl, $[\alpha]^{21}_D$ −16° in H_2O. (II) is converted (cf. A., 1933, 1074) into *l*-methionine, identical with the natural substance; (I) yields d-*methionine*, $[\alpha]^{26}_D$ +8° in H_2O, $[\alpha]^{25}_D$ −22° in 0·2*N*-HCl. E. W. W.

Iodometric determination of cysteine. T. F. Lavine (J. Biol. Chem., 1935, **109**, 141—145).—Cystine (I) is stable to I when in a solution of *N*-HCl and *N*-KI. The indirect iodometric determination of cysteine at room temp. is accurate to ±0·5%, and is consistent with its oxidation to (I) (cf. A., 1933, 266; 1934, 434). E. W. W.

Mineral salts of carbamide. L. Palfray (Compt. rend., 1935, **200**, 1051—1053).—$CO(NH_2)_2$ (2 mols.) with conc. H_2SO_4 (1 mol.) at room temp. gives $2CO(NH_2)_2$,H_2SO_4, and with excess of HBr below 75° it gives the *salt* $2CO(NH_2)_2$,HBr; equimol. amounts in Et_2O at room temp. give $CO(NH_2)_2$,HBr. $CO(NH_2)_2$,HI is also described. These salts are very deliquescent, and at 80° decompose to give NH_4 salts. J. L. D.

Dissociation of carbamide in dilute solution. —See this vol., 702.

Electrolytic reduction of αα′-dicyano-ββ-dimethylglutarimide. G. G. Gratton and G. R. Ramage (J.C.S., 1935, 539).—This gives a poor yield of the *lactam*, m.p. 194°, of δ-*amino*-α*y*-*dicyano*-ββ-*dimethylvaleric acid*, which with conc. HCl at 130—140° gives (?)6-*hydroxy*-3(or 5)-*carbamyl*-2 : 4-*dimethylpyridine*-5(or 3)-*carboxylic acid*, decomp. > 360°. R. S. C.

Silver derivatives of thiosemicarbazide and of thiosemicarbazones. V. Harlay (Compt. rend., 1935, **200**, 1220—1221).—NH_2·CS·NH·NH_2 (I) with $AgNO_3$ in equimol. amounts gives a cryst. *compound*, [AgS·C(NH_2):N·NH_2]HNO_3 (cf. A., 1902, i, 572), converted by NaCl into the *chloride*. (I) (3 mols.) with $AgNO_3$ (2 mols.) affords another Ag derivative. These are stable to light. Acetonethiosemicarbazone (II) with excess of $AgNO_3$ gives an amorphous product, unstable to light. (II) (2 mols.) with $AgNO_3$ (1 mol.), and (II) (3 mols.) with $AgNO_3$ (2 mols.), give cryst. and stable products. Benzaldehydethiosemicarbazone affords analogous products, which combine with one another to form a stable substance. J. L. D.

Maleo- and fumaro-nitriles. J. de Wolf and L. van de Straete (Bull. Acad. roy. Belge, 1935, [v], **21**, 216—225).—Me_2 maleate with saturated NH_3–H_2O at 10° in the dark gives malediamide (I) (cf. A., 1927, 652) and some fumaramide. (I) with P_2O_5 gives *maleonitrile*, m.p. 92·6—93° (A., 1913, i, 253), and a substance, m.p. 48—54°. J. L. D.

Citracono- and mesacono-nitriles. L. van de Straete (Bull. Acad. roy. Belge, 1935, [v], **21**, 226—235).—Citracon- and mesacon-amide (A., 1882, 1281) when heated with P_2O_5 give *citracono-*, m.p. 106·3—106·5°, and *mesacono-nitrile*, b.p. 66°/10 mm., respectively, the latter of which with conc. H_2SO_4 at room temp., or with H_2O_2, gives a *product*, m.p. 147—148°. J. L. D.

Properties and structure of maleo- and citracono-nitriles. P. BRUYLANTS (Bull. Acad. roy. Belg., 1935, [v], **21**, 138—146).—From a discussion of differences in the *d*, *n*, and mol. refractions of maleo- and fumaro- and of citracono- and mesacono-nitriles, and a comparison with the small differences in the corresponding vals. for the respective Me esters, it is suggested that an " internal dinitrile " is formed by the elimination of $2H_2O$ from two amido-groups. N. M. B.

Determination of selenocyanides.—See this vol., 718.

Hydrides of boron. IV. Methyl derivatives of diborane. H. I. SCHLESINGER and A. O. WALKER (J. Amer. Chem. Soc., 1935, **57**, 621—625; cf. A., 1933, 1257).—The prep. of the following *compounds* is described: B_2H_5Me (I), $B_2H_4Me_2$ (II) (m.p. −150·2°), $B_2H_3Me_3$ (III) (m.p. −122·9°), $B_2H_2Me_4$ (IV) (m.p. −72·5°), $BMe_2{\cdot}OH$ (V). The v.d. and v.p. have been measured. The reactions with H_2O indicate that (IV) has a symmetrical structure, that in (II) both Me are attached to the same B, and that in (III) two Me groups are attached to one B and one Me to the other B. (V) is formed by reaction of (I), (III), and (IV) with H_2O. No indication of the formation of B_2HMe_5 or B_2Me_6 was observed. E. S. H.

Formation of organo-metalloidal compounds by micro-organisms. III. Methylated alkyl- and dialkyl-arsines. F. CHALLENGER and L. ELLIS (J.C.S., 1935, 396—400; cf. A., 1934, 278).—Strain *A* (I) (cf. A., 1933, 266) growing on sterile bread crumbs containing diethylarsinic acid (II) evolves a gas which with Biginelli's solution (III) affords $AsMeEt_2,2HgCl_2$, m.p. 196—198°, decomp. 201°, and with HNO_3 and then Na picrate (IV) in H_2O, $OH{\cdot}AsMeEt_2{\cdot}O{\cdot}C_6H_2(NO_2)_3$, m.p. 134—135°. Similarly the mould gas from *n*-propylarsinic acid with (III) affords $AsMe_2Pr^n,2HgCl_2$, m.p. 195°, decomp. 200°, and with CH_2PhCl and (IV) affords *benzyldimethyl-n-propylarsonium picrate*, m.p. 113—114°, and with HNO_3 and (IV) and H_2O, *hydroxydimethyl-n-propylarsonium picrate*, m.p. 143—144°, whilst that from allylarsinic acid with (III) affords $AsMe_2{\cdot}C_3H_5,2HgCl_2$, m.p. 208—209° (decomp.) (m.p. depends on rate of heating), and with CH_2PhCl and (IV), *benzyldimethylallylarsonium picrate*, m.p. 96—97°. The mould does not reduce the double linking of the allyl group. The products from the mould gases were also obtained from synthetic arsines. The following substances are described: $AsMe_2Pr^n,HgCl_2$, m.p. 126—128°; $AsMeEt_2$, b.p. 112—114° (no b.p. in lit.) (*monomercurichloride*, m.p. 153—154°); *benzylmethyldiethylarsonium picrate*, m.p. 85—86°, and *styphnate*, m.p. 89—90°; $AsEt_3,HgCl_2$, m.p. 161—162° (lit. 163—164°); *benzyltrimethylstibonium picrate*, m.p. 183—185°; $AsMe_2{\cdot}C_3H_5$ (V), b.p. 108—109° (lit., b.p. about 160°) (*monomercurichloride*, m.p. 120—121°); *trimethylallylarsonium iodide*, m.p. 184—186°. (V) with limited access of air gave a product from which cacodylic acid (VI) and *hydroxydimethylallylarsonium picrate*, m.p. 159—160°, were isolated. Similarly $AsMe_3$ (improved prep.) gives (VI) and hydroxytrimethylarsonium picrate, whilst $AsEt_3$ gives (II) (A., 1930, 330). Growth of (I) on bread and on aq. media containing K Sb tartrate gives no odour of alkylstibine. H. G. M.

Synthesis of halides of tin alkyls. K. A. KOTSCHESCHKOV (J. Gen. Chem. Russ., 1934, **4**, 1359—1363).—$SnCl_4$ and MgEtBr in Et_2O affords a mixture of $SnEt_3Cl$ (I), $SnEt_2Cl_2$ (II), and $SnEt_4$ (III). (III) and $SnCl_4$ (2 hr.; 200°) yield (II), which with (III) gives (I); the corresponding bromides are prepared analogously. R. T.

Processes of dehydrogenation. II. Action of selenium or palladised charcoal on *cyclo*pentane derivatives at elevated temperature. L. RUZICKA and E. PEYER (Helv. Chim. Acta, 1935, **18**, 676—684).—Chrysene does not appear to be formed when 3-methyl*cyclo*pentenophenanthrene is heated with Se or Pd–C at 450°, but the results are not regarded as final, on account of the small amount of available material. The fundamental possibility of the enlargement of a 5-C to a 6-C ring is established by the ready conversion of 1- or 2-methylhydrindene into $C_{10}H_8$ by Se or Pd–C at 450°, whereas at 350° or 400° the hydrocarbons remain unchanged. Similarly $C_{10}H_8$ is produced from 1- and 2-ethylhydrindene, 1-iso*octylhydrindene* (I), b.p. 100—102°/0·2 mm., 153°/12 mm., and *methylisopropylhexahydrofluorene* (II), b.p. 105°/0·6 mm., about 150°/10 mm., or from 1 : 2-*diethyl*-Δ^1-cyclo*hexene*, b.p. 54—55°/10 mm., and Se at 420°. The yields of $C_{10}H_8$ vary from 5% to 50%, and are generally twice as great with Se as with Pd–C; they are maximal with Me derivatives, and diminish with the complexity of the hydrocarbon. If secondary reactions are to be avoided, the temp. of dehydrogenation must not therefore exceed 350°. The formation of aromatic from 5-membered rings above 400° does not invariably occur in an obvious manner, since elimination of groups occurs to a marked extent under these conditions. Indene derivatives in presence of Se or Pd–C at about 350° pass smoothly into almost homogeneous hydrindene derivatives, a part of the initial hydrocarbon being lost. The hydrogenation of the unsaturated 5-membered ring under conditions of dehydrogenation renders improbable the formation of methyl*cyclo*pentadienophenanthrene from sterol or bile acid derivatives. Treatment of Me *iso*hexyl ketone with indene and KOH in boiling MeOH gives *methylisohexylbenzofulvene*, b.p. about 120°/0·2 mm., hydrogenated to (I), also obtained from *methylisohexenylbenzofulvene* (III), b.p. about 130°/0·2 mm. (III) is converted by 100% HCO_2H at 140° into *methylisopropylfluorene*, b.p. 105°/0·3 mm., hydrogenated (PtO_2 in MeOH) to (III). H. W.

Purification of the common carotenoids and the quantitative measurement of their absorption spectra. E. S. MILLER (Bot. Gaz., 1935, **96**, 447—467).—Improved methods are described and spectrographic data are given for α- and β-carotene, xanthophyll, and lycopene. The customary spectroscopic tests of purity are only approx. Detailed examination of absorption spectra affords the most trustworthy test. A quant. spectral method of analysis of binary mixtures of carotenoids is described. A. G. P.

Directive influence of electric moment on substitution in the benzene ring.—See this vol., 684.

Kinetics of the electrochemical chlorination of benzene.—See this vol., 709.

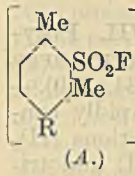
Preparation of hexaiodobenzene. J. F. Durand and (Mlle.) M. Mancet (Bull. Soc. chim., 1935, [v], **2**, 665—666).—Conditions for the prep. of C_6I_6 in 81% yield from C_6H_6–61·5% oleum–I at 170—180° are given. The yield is largely dependent on the oleum concn. J. W. B.

Condensation of *iso*propyl alcohol with toluene and its nitro-derivatives. G. Desseigne (Bull. Soc. chim., 1935, [v], **2**, 617—623).—Addition of $Pr^{\beta}OH$ to PhMe–78% H_2SO_4 at 70—100° and isolation of the product by steam distillation at 160° affords an 82% yield of *p*-cymene (I), together with small amounts of 2 : 4-*di*- (II), b.p. 225°/770 mm. (14%), and 2 : 4 : 6-*tri*-iso*propyltoluene*, b.p. 252—253°/757 mm. The proportion of (I) is decreased to 38% and that of (II) is increased to 47% when 95% H_2SO_4 is used. Similar condensation of $Pr^{\beta}OH$ and *o*-$C_6H_4Me{\cdot}NO_2$ with 92—93% H_2SO_4 at 35—40° affords 2-nitro-*p*-cymene (reduced to the 2-NH_2-derivative), identical with the nitration product from (I), and 2-*nitro*-4 : 6-*di*iso*propyltoluene*, b.p. 158°/15 mm., reduced (Clemmensen) to the 2-NH_2-derivative, b.p. 141°/11 mm. (*Ac* derivative, m.p. 118°; *hydrochloride*, m.p. 226—228°). Similarly *p*-$C_6H_4Me{\cdot}NO_2$ at 70—80° affords 4-*nitro*-*o*-*cymene*, b.p. 144—145°/15 mm. [reduced to the 4-NH_2-compound, b.p. 123°/15 mm. (*Ac* derivative, m.p. 103°; *hydrochloride*, m.p. 233°)], and 4-*nitro*-2 : 6-*di*iso*propyltoluene*, b.p. 168°/11 mm., m.p. 61°, reduced to the 4-NH_2-compound, b.p. 146°/11 mm. (*Ac* derivative, m.p. 162°; *hydrochloride*, m.p. 245—247°). J. W. B.

Organic magnesium compounds. I. Reaction between phenyl *p*-toluenesulphonate and magnesium phenyl bromide in various solvents. K. Mine (J. Chem. Soc. Japan, 1934, **55**, 905—909).—Et_2O, *iso*amyl ether, C_6H_6, PhMe, and xylene are used as solvents. Ch. Abs. (*r*)

Chlorinated derivatives of *p*-xylene. H. Wahl (Compt. rend., 1935, **200**, 936—938).—From chloro-*p*-xylidines by the Sandmeyer reaction, 2 : 3-*dichloro*- (I), m.p. −2°, b.p. 230°, and 2 : 6-*dichloro*- (III), m.p. 15°, b.p. 222°/770 mm., -p-*xylene*, and 2 : 5-dichloro-*p*-xylene (III) are prepared. (I) and (II) are readily sulphonated by H_2SO_4, and from (I) a *sulphonyl chloride* (IV), m.p. 62°, *sulphonamide* (V), m.p. 201°, and *sulphonanilide* (VI), m.p. 157°, and from (II) a *sulphonyl chloride*, m.p. 81°, *sulphonamide*, m.p. 150°, and *sulphonanilide*, m.p. 175°, are prepared. (III) is sulphonated only by oleum (decomp.), yielding a *K sulphonate*, from which a *sulphonyl chloride*, m.p. 71°, *sulphonamide*, m.p. 165°, and *sulphonanilide*, m.p. 171°, are obtained. When the fraction of b.p. 220—230° from the chlorination (VII) of *p*-xylene is treated with H_2SO_4, it yields a *Ca sulphonate* from which (IV), (V), and (VI) are prepared, and, by hydrolysis (I). (I) is therefore obtained, as well as (III), during (VII). E. W. W.

Action of Grignard reagents on aromatic sulphonyl fluorides. D. T. Gibson (J. pr. Chem., 1935, [ii], **142**, 218—222).—A criticism of Steinkopf *et al.* (A., 1934, 1341). The calc. composition for the compounds $C_{17}H_{18}O_6S_4F_2$, m.p. 135° and m.p. 272° (from *m*-xylene-2 : 4-disulphonyl fluoride and MgMeI),



(*A.*)

is incorrect. The analytical data agree better with $C_9H_{11}O_4FS_2$ (*A*, R=SO_2Me; *n*=1), m.p. 135°, and $C_{17}H_{19}O_8S_4F$ (*A*, R=$SO_2{\cdot}$; *n*=2), m.p. 272°. Only sulphonyl fluorides (I) give bis-sulphonylmethane derivatives (II) with Grignard reagents. $PhSO_2Me$ and MgMeI in boiling xylene give PhSH; $PhSO_2F$ and MgEtI give bisphenylsulphonylethane. Addition of $PhSO_2{\cdot}CH_2Cl$ to the product ($PhSO_2{\cdot}MgI$) of interaction of $PhSO_2F$ and MgEtI affords a Cl-containing compound, m.p. 138°, readily converted by Na_2SO_3 into bisphenylsulphonylmethane (III). Hence the initial product of interaction between (I) and MgRX is probably $PhSO_2{\cdot}CH_2F$. *p*-$C_6H_4Me{\cdot}SO_2F$ and MgMeI give bis-*p*-tolylsulphonylmethane, but with $MgPr^{\beta}I$, di-*p*-tolyldisulphone results. Hence it is suggested that the formation of (II) is due to the intermediate compound $(PhSO_2F{\rightarrow}H)_2CH{\cdot}MgI$ resulting from the sp. co-ordinating power of F. The yield of (III) from $PhSO_2F$ and MgMeI decreases greatly if excess of the Grignard reagent is used. J. W. B.

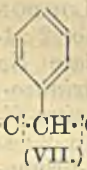
Action of Grignard reagents on aromatic sulphonyl fluorides. W. Steinkopf (J. pr. Chem., 1935, [ii], **142**, 223—224).—A reply to Gibson (preceding abstract). The formula given for the compound, m.p. 272°, from *m*-xylene-2 : 4-disulphonyl fluoride (A., 1934, 1341) was an error for $C_{17}H_{20}O_7S_4F_2$, with which the analytical data agree. J. W. B.

2 : 4-Dinitrodiphenylsulphones. J. D. Loudon (J.C.S., 1935, 537—539).—2 : 4-$C_6H_3Cl(NO_2)_2$ or 2 : 4-$(NO_2)_2C_6H_3{\cdot}SO_2C_6H_4Me$-*p* with the appropriate Na sulphinate in hot aq. EtOH give 2 : 4 : 3′-*trinitro*-, m.p. 196—197°, and 2′ : 5′-*dichloro*-2 : 4-*dinitro-diphenylsulphone*, m.p. 178°, and seven known 2 : 4-dinitrophenylsulphones. 4′-Chloro- (I) and -bromo-2 : 4-dinitrodiphenylsulphone with KNO_3–H_2SO_4 give the 2 : 4 : 3′-(NO_2)$_3$-derivatives, m.p. 203° (II) and 210° (III), respectively. The sulphones are cleaved by piperidine (IV) to yield 2 : 4-dinitropiperidinobenzene. (II) or (III) with (IV) in dioxan gives 2 : 4 : 3′-trinitro-4′-piperidinodiphenylsulphone; the Cl is thus reactive, but *p*-$C_6H_4Cl{\cdot}SO_2Na$ and (II) give (I), apparently by exchange of aryl groups. A similar exchange is effected when most of the above sulphones are heated with an excess of a Na sulphinate in dioxan, the NO_2-free nucleus being exchanged. Similarly 2 : 4-dinitrodiphenylsulphone with *p*-tolyl or Me *p*-toluenethiolsulphonate and a little Na_2CO_3 in dioxan give 2 : 4-dinitrophenyl-*p*-tolylsulphone. R. S. C.

Polymerisation of styrene, citral, and heptaldehyde. H. E. Thompson and R. E. Burk (J. Amer. Chem. Soc., 1935, **57**, 711—713).—Highly purified citral and heptaldehyde are stable in absence of O_2; polymerisation normally occurs with absorption of 1 and 2 O, respectively. The rate of polymerisation of styrene (I) is very greatly reduced by careful purification and absence of O_2, but is still governed by the presence of catalysts (already present or added);

normal polymerisation of (I) involves absorption of about 0·33 O, but no increase in mol. wt., and only a trace of non-volatile solid is observed. R. S. C.

Highly-polymerised compounds. CVII. Polystyrenes. H. STAUDINGER and A. STEINHOFER (Annalen, 1935, **517**, 35—53; cf. A., 1934, 879).—At 400—500°/1 atm. polystyrene (I) is rapidly converted into $CHPh{:}CH_2$ and distyrene fractions (II), whilst at 310—350° larger amounts of (II) and tristyrene fractions (III) slowly result. If reaction is conducted in high vac., tetrastyrene fractions (IV) are also isolated. (II), (III), and (IV) contain much unsaturated (V) and little saturated (VI) hydrocarbons. (V) cannot be obtained homogeneous and are identified by their derivatives. (VI) are isolated by further polymerisation of (V) and subsequent distillation. (II) contains *αγ-diphenylpropane*, b.p. 155—157°/12 mm., and *αγ-diphenyl-Δ$^{\gamma}$-butene*, oxidised to $COPh{\cdot}CH_2{\cdot}CH_2Ph$, m.p. 72—73°. (III) is composed of (?) *αγε-triphenylpentane*, b.p. 170—172°/0·5 mm. [also obtained from $CO(CH_2{\cdot}CH_2Ph)_2$ and MgPhBr followed by dehydration of the carbinol $OH{\cdot}CPh(CH_2{\cdot}CH_2Ph)_2$ and hydrogenation (colloidal Pd) of the unsaturated hydrocarbon], and *αγε-triphenyl-Δ$^{\epsilon}$-hexene*, oxidised to *Ph βδ-diphenyl-n-butyl ketone*, m.p. 80—81° (*oxime*, m.p. 123—124°), also obtained by hydrogenation of β-phenyl-β-styrylpropiophenone. These results show that (I) is $\cdot\cdot[\cdot CHPh{\cdot}CH_2\cdot]_n\cdot\cdot$ and that cracking occurs according to the schemes, $\cdot\cdot[\cdot CHPh{\cdot}CH_2]_n\cdot\cdot \longrightarrow CH_2Ph{\cdot}CH_2{\cdot}CPh{:}CH_2 + CH_2Ph{\cdot}CH_2{\cdot}CPh{:}CH_2$ and $\longrightarrow CH_2Ph{\cdot}CH_2{\cdot}CH_2Ph + CH_2{:}CPh{\cdot}CH_2{\cdot}CPh{:}CH_2$. The instability of (I) is ascribed to the presence of the allyl group [cf. (VII)]. It is proposed to designate the "double linking rule" of cracking the allyl grouping rule. The polymerisation of $CHPh{:}CH_2$ is a chain process interrupted by a secondary change which occurs with increasing frequency as the rate of polymerisation increases. A condensation process is excluded (cf. Whitby *et al.*, A., 1928, 627), since the double linking of the higher polymerides is too sluggish and simpler products do not accompany the more complex in the final material. It appears probably that a double linking, due to wandering of H, is present in the terminal group of (I); its determination is not suitably effected by titration with Br, since substitution accompanies addition. The prep. of hemicolloidal products by controlled cracking of complex (I) is described, a higher temp. being required for degradation as the process proceeds. The prep. of (I) with definite terminal groups has been attempted. (I) obtained in presence of conc. H_2SO_4 which gives relatively very simple products are entirely hydrocarbons. Similarly, cracking of (I), mean mol. wt. 125,000, in *cyclo*hexane at 250° in presence of HI, AcOH, Ac_2O, $CHCl_3$, or piperidine leads to products which do not contain halogen, Ac, or N. Hemicolloidal products with foreign terminal groups are not formed when $CHPh{:}CH_2$ is heated at 100° under N_2 with AcOH, Ac_2O, $CHCl_3$, piperidine, MeOH, or MeOH+5%HCl. Hydrocarbons are the sole products of the polymerisation of $CHPh{:}CH_2$ at 250° in *cyclo*hexane containing HI, Ac_2O, AcOH, $CHCl_3$, or piperidine. H. W.


·C·CH·C·
(VII.)

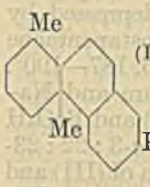
Highly-polymerised compounds. CVIII. Viscosity of solutions of cyclic compounds. H. STAUDINGER and A. STEINHOFER (Annalen, 1935, **517**, 54—66).—Determination of $\eta_{sp.}$ (1·4%) of CH_2Ph_2, $(CH_2Ph)_2$, $CH_2(CH_2Ph)_2$, $(\cdot CH_2{\cdot}CH_2Ph)_2$, $CH_2(CH_2{\cdot}CH_2Ph)_2$, $(\cdot CH_2{\cdot}CH_2{\cdot}CH_2Ph)_2$, and $CH_2([CH_2]_4Ph)_2$ in C_6H_6 and CCl_4, of hexa- and octadecylbenzene in C_6H_6, of di*cyclo*hexyl-αδ-butane, -αε-pentane, and -αζ-hexane in C_6H_6 and CCl_4 and of Ph and *cyclo*hexyl myristate, palmitate, and stearate in C_6H_6 and CCl_4 shows that the increment for the Ph or cyclo*hexyl* group in C_6H_6 or CCl_4 is approx. $4{\cdot}0\times10^{-3}$, being identical for each within the experimental limits. $\eta_{sp.}$ of substances with thread mols. depends mainly on the length of the mol. and the concn. of the solution, and is scarcely affected by differences in structure which cause profound differences in chemical and other physical properties. Thus *dihexyl terephthalate*, b.p. 235°/13 mm., m.p. 37°, and *diheptylquinol*, b.p. 286°/13 mm., m.p. 60—60·5°, have the same $\eta_{sp.}$ The presence of a single Ph group in the side-chain of a compound causes an increase in viscosity of $4{\cdot}5\times10^{-3}$ in C_6H_6 and $7{\cdot}0\times10^{-3}$ in CCl_4 as shown by comparison of $CH_2([CH_2]_4Ph)_2$ and $CHPh([CH_2]_4Ph)_2$, $CH_2([CH_2]_2Ph)_2$ and $CHPh([CH_2]_2Ph)_2$, $Ph[CH_2]_4Bz$ and $Ph[CH_2]_2{\cdot}CHPh{\cdot}CH_2Bz$, $Ph[CH_2]_7Ph$ and $CH_2(CHPh{\cdot}[CH_2]_2Ph)_2$. Comparison of $CH_2([CH_2]_4Ph)_2$ with $CO([CH_2]_4Ph)_2$, $CH_2([CH_2]_2Ph)_2$ with $CO([CH_2]_2Ph)_2$ and $Ph[CH_2]_4{\cdot}COPh$, and $Ph[CH_2]_3Ph$ with $Ph[CH_2]_2{\cdot}OPh$ shows that $\eta_{sp.}$ of ketones is identical with that of hydrocarbon in CCl_4 but somewhat greater in C_6H_6. Saturated and unsaturated ketones have identical $\eta_{sp.}$ (examples $Ph[CH_2]_2{\cdot}CHPh{\cdot}CH_2Bz$ and $CHPh{:}CH{\cdot}CHPh{\cdot}CH_2Bz$) but the increment for a conjugated double linking is $2{\cdot}5\times10^{-3}$ in C_6H_6 and 4×10^{-3} in CCl_4 [examples: $CH_2Ph{\cdot}CH_2Bz$ and $CHPh{:}CHBz$; $CO([CH_2]_2Ph)_2$ and $CO(CH{:}CHPh)_2$; $Ph[CH_2]_4Bz$ and $CHPh{:}CH{\cdot}CH{:}CHBz$; $CO([CH_2]_4Ph)_2$ and $CO(CH{:}CH{\cdot}CH{:}CHPh)_2$]. The observed and calc. vals. of a no. of simple polymeric styrenes are in harmony. Determinations of $\eta_{sp.}$ at 20°, 40°, and 60° of a series of the substances described above show that it diminishes with t rather less in C_6H_6 than in CCl_4. *αε0-Triphenylnonane*, b.p. 216—218°/0·04 mm., and *αγεη-tetraphenylheptane*, b.p. 260—262°/3 mm., are new. H. W.

Highly-polymerised compounds. CX. Constitution of polypropenylbenzene and its derivatives. H. STAUDINGER and E. DREHER (Annalen, 1935, **517**, 73—104).—In contrast with styrene and p-$OMe{\cdot}C_6H_4{\cdot}CH{:}CH_2$, propenylbenzene derivatives (I) polymerise with difficulty, eucolloidal products not being available since polymerisation does not occur in absence of catalysts. The introduction of a terminal Me diminishes the tendency of the ethylenic linking towards polymerisation. Aromatic propenyl derivatives polymerise more readily than the corresponding allyl compounds, thus giving a possible method of separation. Polymerisation of (I) is a chain reaction occurring in the αγ-position (instead of

αβ as with other ethylenic compounds) owing to the mobility of H in Me as a consequence of the allyl group. (I) is therefore · · · [CHPh·CH_2·CH_2]$_x$ · · ·, but the nature of the terminal groups is undecided. Proof is furnished by the isolation of αδ-diphenyl-$\Delta^{\alpha\gamma}$-butadiene, m.p. 148°, and αδ-*pp'*-dimethoxydiphenylbutadiene, m.p. 221—223°, from the products of the cracking of polypropenylbenzene (II) and polyanethole, respectively. (II) are hemicolloidal, white products without distinctive m.p., sol. without swelling in various media to solutions of low viscosity which follow the Hagen–Poiseuille law. Cryoscopic determinations of the mol. wt. of (II) and their OEt-derivatives in C_6H_6 and *cyclo*hexane give results in harmony with those obtained from measurements of $\eta_{sp.}$ but this is not the case with the OMe-compounds. In freezing $C_{10}H_8$ Δ is greater as the complexity of (II) (as measured in C_6H_6 or *cyclo*hexane and by determination of viscosity) increases; in the case of the most complex fractions the mol. wt. 240 is indicated. The material recovered from such solutions is identical with the original, and the results are considered abnormal, since they do not harmonise with all other available chemical and physical evidence. Possibly the $C_{10}H_8$ mols. suffer reversible change due to the solute. Measurements of $\eta_{sp.}$ in C_6H_6 and $C_{10}H_8$ are recorded. $\eta_{sp.}$ of (II) and of polystyrenes is the same in C_6H_6 as in *m*-cresol, whereas for poly-*p*-methoxystyrenes, poly-*p*-methoxy- and -ethoxy-propenylbenzenes the vals. are higher in *m*-cresol than in C_6H_6. This is attributed to the formation of oxonium salts, thus confirming the assumption made previously in the analogous case of the cellulose Me ethers (III) and cellulose acetates (IV). When due allowance is made for this complication, it is shown that the transformation of (IV) into (III) is accomplished without change in the degree of polymerisation, thus giving further important evidence of the macro-mol. structure of cellulose. H. W.

Higher benzenoid hydrocarbons. Syntheses with the aid of metallo-derivatives. H. F. Miller and G. B. Bachman (J. Amer. Chem. Soc., 1935, **57**, 766—771).—9-Chlorofluorene (I) reacts with Grignard reagents by double coupling to form bisdiphenylenethane (II) and dialkyl when the reagent exists mainly as MgR_2, but gives 9-alkylfluorenes when much MgRX is present. Solvents which influence the equilibrium, $2MgRX \rightleftharpoons MgR_2 + MgX_2$, thus influence also the course of the reaction. Li 9-fluorenyl (III) is often more useful for syntheses than Mg 9-fluorenyl bromide (IV). Other Grignard reactions with fluorene (V), anthracene, and phenanthrene are reported. Mg 9-phenanthryl bromide (prep. from 9-bromophenanthrene in 92—93% yield) with the appropriate reagent in Et_2O–C_6H_6 gives 9-n-*propyl*- (47%), m.p. 74°, b.p. 265—270°/22 mm. (*picrate*, m.p. 134°), 9-n-*butyl*- (52%), m.p. 58°, b.p. 282—284°/20 mm. (*picrate*, m.p. 99·5°), and 9-*acetyl-phenanthrene* (27%), m.p. 73—74° (*picrate*, m.p. 107°; *oxime*, m.p. 154—155°), and with $CH(OEt)_3$ phenanthrene-9-aldehyde (46% yield), m.p. 99—100° (*acetal*, m.p. 79—80°; oxime, m.p. 156—157°). (IV), prepared in 32% yield from (V) and MgEtBr in xylene and isolated by its insolubility in Et_2O, does not react in xylene with Pr$^{\alpha}$Br or Bu$^{\alpha}$Br, but with CH_2Ph·MgBr gives $(CH_2Ph\cdot)_2$ and (II), and with AcCl gives 9-acetylfluorene (58% yield), m.p. 107° (*oxime*, m.p. 167°), and with $CH(OEt)_3$ an amorphous polymeride. (III), obtained in 80% yield from (V) and LiBu or LiMe, with Bu$^{\alpha}$Br, AcCl, and $CH(OEt)_3$ affords 9-n-*butyl*- (41%), m.p. 101°, b.p. 192—195°/33 mm., and 9-*acetyl-fluorene* (60%), m.p. 107°, and an amorphous polymeride, respectively. (I) with MgPhBr, *n*-C_5H_{11}·MgBr, or MgBu$^{\alpha}$Br in Et_2O or C_6H_6 gives 95% yields of (II); with Mg *cyclo*hexyl bromide in Et_2O it gives 93% of (II), but in C_6H_6 70% of (II) and 20% of 9-*cyclohexylfluorene*, m.p. 102—103°; MgEtI in Et_2O gives 20% of (II) and 65% of 9-ethylfluorene, m.p. 106—107° (lit. an oil), b.p. 160—165°/10 mm. Grignard reagents could not be prepared from 9 : 10-dihydroanthracene (prep. in 76% yield by Na in liquid NH_3), 9-bromoanthracene, m.p. 100°, 2-bromofluorene, m.p. 110°, or 3-bromoacenaphthene (cf. lit.), m.p. 52°, b.p. 204—209°/30 mm., 327—332°/760 mm. R. S. C.

Polyterpenes and polyterpenoids. XCVI. Constitution of fichtelite. L. Ruzicka and E. Waldmann (Helv. Chim. Acta, 1935, **18**, 611—612; cf. A., 1923, i, 819).—Dehydrogenation of fichtelite (I), m.p. 46° (Pd–C at 330—370°), affords H_2 and CH_4 (8 : 1 by vol.). (I) is therefore a dimethyl*iso*propylperhydrophenanthrene in which only the position of Me lost during hydrogenation is uncertain. (I) has probably the annexed constitution.



(I.)

H. W.

1 : 2-Benzpyrene. L. F. Fieser and M. Fieser (J. Amer. Chem. Soc., 1935, **57**, 782—783; cf. Cook *et al.*, A., 1933, 601).—The prep. of 1 : 2-benzpyrene (I), m.p. 176·5—177°, from pyrene is modified to give a 36% over-all yield. 1′ : 2′ : 3′ : 4′-*Tetrahydro*-1 : 2-*benzpyrene*, m.p. 113° (*picrate*, m.p. 166°), is best (84%) prepared by hydrogenation (200°/3000 lb.; Cu chromite in EtOH) of the tetrahydro-ketone (II) and is best removed from impure (I) by Se-dehydrogenation. (II) with MgMeI in C_6H_6 gives 4′-*methyl*-1′ : 2′-*dihydro*-1 : 2-*benzpyrene* (73% yield), m.p. 155—156°, which with Se at 330° gives 4′-*methyl*-1 : 2-*benzpyrene*, m.p. 217·5—218° (*picrate*, m.p. 203—204°).

R. S. C.

Syntheses of polycyclic compounds related to sterols. III. 9-Methyl- and 3′ : 9-dimethyl-*cyclo*pentenophenanthrene. D. J. C. Gamble and G. A. R. Kon (J.C.S., 1935, 443—445; cf. A., 1934, 288).—The Grignard reagent from 1 : 4-$C_{10}H_6BrMe$ with $(CH_2)_2O$ in Et_2O give α-(4-*methyl*-1-*naphthyl*)*ethyl alcohol* (I), b.p. 135°/0·5 mm., m.p. 60° (*picrate*, m.p. 107°), and with CO_2 1 : 4-$C_{10}H_6Me$·CO_2H, oxidised to 1 : 4-$C_{10}H_6(CO_2H)_2$. (I) with HBr at 100° affords the *bromide*, m.p. 45—46°, b.p. 142°/0·5 mm. (*picrate*, m.p. 72—73°; unstable), the Grignard reagent (II) of which with 2-methyl*cyclo*pentanone gives αδ-*di*-(4-*methyl*-1-*naphthyl*)*butane*, m.p. 126—127°, b.p. about 230°/0·4 mm. {*dipicrate*, m.p. 174—175°; [s-$C_6H_3(NO_2)_3]_2$ compound, m.p. 192—193°}, and a carbinol, dehydrated by P_2O_5 at 140° to 1 : 9-*dimethyl*-1 : 2-*cyclopentano*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, b.p. 160°/0·5 mm., which affords (Se; 290—300°) 9-*methyl*-1 : 2-

cyclo*pentenophenanthrene* (III), m.p. 109—110° [*picrate*, m.p. 153—154°; s-$C_6H_3(NO_2)_3$, m.p. 170—171°, and $C_6H_2Me(NO_2)_3$ compound, m.p. 135—136°; *styphnate*, m.p. 190—191°]. 2 : 5-Dimethylcyclopentanone and (II) lead to 2 : 5-*dimethyl*-1-β-(4-*methyl*-1-*naphthyl*)*ethyl*cyclo*pentan*-1-*ol*, b.p. 185—190°/0·5 mm., 1 : 9 : 3′-*trimethyl*-1 : 2-cyclo*pentano*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, b.p. 170°/0·6 mm., and 9 : 3′-*dimethyl*-1 : 3-cyclo*pentenophenanthrene* (IV), m.p. 80° [*picrate*, m.p. 134—135°; s-$C_6H_3(NO_2)_3$, m.p. 149—150°, and $C_6H_2Me(NO_2)_3$ compound, m.p. 113—114°; *styphnate*, m.p. 159—160°]. The 3′-Me analogue (V) of (II) gives a *styphnate* (VI), m.p. 135—136°. The non-identity of (III) or (IV) with (V) confirms the now accepted structure of strophanthidin and uzarigenin. The impure styphnate of *cyclo*pentenophenanthrene has m.p. 154°, but does not depress the m.p. of (VI). R. S. C.

Hydrocarbons from neoergosterol. G. A. Haslewood and (Miss) E. Roe (J.C.S., 1935, 465—467).—22-Dihydroneoergosterol (I), m.p. 141—143° (lit. 140°), from neoergosterol (II) in Et_2O or its acetate in $COMe_2$ and H_2–Pd-black, and its 3 : 5-dinitrobenzoate, m.p. 216—218°, do not depress the m.p. of (II) and its ester, respectively. (I) with $KHSO_4$ gives *neoergostatetraene* (III), m.p. 63—64°, depressed by neoergostatriene (IV) but not by neoergostapentaene (V), but with P_2O_5 a *dimeride*, $C_{54}H_{80}$, m.p. 187—190°. Dehydrogenation of (III) gives a mixture and Na–C_5H_{11}·OH does not effect reduction. (II) and BzO_2H give a product, hydrolysed to *neoergosta*-3 : 22 : 23-*triol*, m.p. 202—204°. Absorption spectra of (III) and (V) are very similar, but differ from that of (IV), indicating that the fifth ethylenic linking of (V) is in the side-chain and that the fourth of (III) and (V) is in ring I conjugated with an aromatic ring II, and thus supporting the allocation of the nuclear ethylenic linkings of ergosterol to ring II. R. S. C.

Organic compounds of sulphur. XXV. Interaction between organic azides and aromatic thioketones and a new method of converting the azido-group into the amino-group. A. Schönberg and W. Urban (J.C.S., 1935, 530—532).—RN_3 and $CR'_2{:}S$ [R=Ph, α-$C_{10}H_7$, CH_2Ph, SO_2Ph; R′$_2$=Ph_2, *pp*′-$(C_6H_4{\cdot}OMe)_2$, $C_6H_4{\cdot}O{\cdot}C_6H_4$] heated together in N_2 give $RN{:}CR'_2$, whence the amine can be obtained. *Benzenesulphonimidoxanthen*, m.p. 165—166°, is described. PhN_3 does not react with $CPh_2{:}O$. F. R. G.

Activity of mixed catalysts in the simultaneous dehydration of (I) ethyl alcohol and ammonia, (II) ethyl alcohol and aniline. Catalytic preparation of ethylaniline. I. I. Schujkin and A. A. Balandin (J. Gen. Chem. Russ., 1934, **4**, 1444—1450, 1451—1457).—I. [With Z. I. Plotkin.] The yield of amines obtained by passing EtOH–NH_3 over various catalysts at 300—400° diminishes in the order Al_2O_3=10 : 1, Al_2O_3–Fe_2O_3 (I) > Al_2O_3–ZnO > Al_2O_3–Cr_2O_3 > Al_2O_3–SnO. Production of gaseous by-products is least with (I). The reactions involved are explained on the basis of the multiplet theory.

II. [With F. T. Dimov.] The yields of NHPhEt and $NPhEt_2$ are greater when Al_2O_3 alone is used as catalyst (350°) than when it contains 5—20% of Fe_2O_3, SnO, Cr_2O_3, NiO, or ZnO. R. T.

Electrolytic reduction of imido-ethers. H. Wenker (J. Amer. Chem. Soc., 1935, **57**, 772).—By electrolytic reduction in 2*N*-H_2SO_4 at 0° of the corresponding imido-ethers are prepared $NH_2{\cdot}CH_2Ph$ (76%), *m*- (76%) and *p*-$C_6H_4Me{\cdot}NHPh$ (94%), NH_2Et (16%), $NH_2{\cdot}CH_2{\cdot}CH_2Ph$ (14%), and p-*ethoxybenzylamine* (66% yield) (*picrate*, m.p. 191°; *hydrochloride*, m.p. 234°). R. S. C.

Preparation of *N*-substituted sulphon-*m*- and -*p*-toluidides. G. H. Young (J. Amer. Chem. Soc., 1935, **57**, 773; cf. this vol., 206).—p-*Toluenesulphon*-N-*methyl*-, m.p. 63°, -*ethyl*-, m.p. 60·5—61°, -n-*propyl*-, m.p. 51°, and -iso*amyl*-m-*toluidide*, m.p. 76·5° (80—98% yields), and p-*toluenesulphon*-N-iso*propyl*-, m.p. 107°, -iso*butyl*-, m.p. 73°, -n-*amyl*-, m.p. 59·5—60°, and -iso*amyl*-p-*toluidide*, m.p. 89·5—90° (60—91% yields), are prepared. R. S. C.

General method of synthesis of the *N*-disubstituted aminoethylenes, CR:CR′·NR″Ar. J. Hoch (Compt. rend., 1935, **200**, 938—940).—$CPhMe(OEt)_2$ heated with NHPhMe forms α-N-*methylanilinostyrene*, b.p. 161—162°/13 mm., which is reduced catalytically to CHPhMe·NPhMe, and hydrolysed (HCl) to COPhMe and NHPhMe. The following are similarly obtained: α-N-*ethylanilino*-, b.p. 167°/12 mm., α-N-*methyl*-p-*toluidino*-, b.p. 167°/10 mm., and α-N-*methyl*-p-*anisidino*-, b.p. 185°/10 mm., -*styrene*; α-N-*methylanilino*-, b.p. 170—171°/12 mm., α-N-*ethylanilino*-, b.p. 175°/10 mm., α-N-*methyl*-p-*toluidino*-, b.p. 181°/12 mm., and α-N-*methyl*-p-*anisidino*-, b.p. 192—194°/9 mm., -p-*methylstyrene*; α-N-*methylanilino*-p-*methoxystyrene*, m.p. 55°, b.p. 190—200°/12 mm. (decomp.), α-N-*methylanilino*-, m.p. 82°, b.p. 230°/10 mm., and α-N-*methyl*-p-*toluidino*-, m.p. 76°, b.p. 232°/10 mm., -*stilbene*; γ-N-*methylanilino*-, b.p. 129—131°/12 mm., and γ-N-*methyl*-p-*anisidino*-, b.p. 166—167°/17 mm., -Δ^{γ}-*heptene*; N-*methylanilino*-, b.p. 140/13 mm., N-*ethylanilino*-, b.p. 152—153°/15 mm., and N-*methyl*-p-*toluidino*-, b.p. 150°/10 mm., -Δ^1-cyclo*hexene*; and β-N-*methylanilino*-, b.p. 205°/16 mm., and β-N-*methyltoluidino*-, m.p. 69°, b.p. 207—208°/12 mm., -*styrene*. E. W. W.

Tetrazotisation of aryl diamines with special reference to *o*-phenylenediamine. H. H. Hodgson and J. Walker (J.C.S., 1935, 530; cf. Schoutissen, A., 1934, 67).—1 : 2 : 4-$C_6H_3Me(NH_2)_2$ and *o*-, *m*-, and *p*-$C_6H_4(NH_2)_2$ in AcOH with $NO{\cdot}SO_4H$, (cf. *ibid.*, 181) give, without secondary reactions, tetrazo-solutions which with Cu_2Cl_2 (Sandmeyer) yield 70% of the theoretical amounts of the Cl_2-derivatives. F. R. G.

Stereochemistry of diphenyls. XXXIX. Synthesis of active 2 : 6-dibromo-3 : 3′-diamino-4 : 4′-ditolyl. W. I. Patterson and R. Adams (J. Amer. Chem. Soc., 1935, **57**, 762—764; cf. A., 1934, 1351).—A Ph_2 derivative, substituted in the 2 : 6- but not in the 2′ : 6′-positions, is resolved. 2-Nitro-*p*-toluidine [prep. in 70% yield from 2 : 4-$C_6H_4Me(NO_2)_2$ and NH_4HS–EtOH] gives (diazo-reaction; 75% yield) 4-iodo-2-nitrotoluene, which

with Cu in hot $PhNO_2$ gives 3 : 3′-dinitro-4 : 4′-ditolyl (39% yield), reduced by NaHS–EtOH to 3-*nitro*-3′-*amino*-4 : 4′-*ditolyl* (60% yield), m.p. 108—109° (*Ac* derivative, m.p. 193·5°). This with Br–AcOH affords 2 : 6-*dibromo*-3′-*nitro*-3-*amino*-4 : 4′-*ditolyl*, m.p. 139° (70% yield) (*Ac* derivative, m.p. 145·5—146°), oxidised by CrO_3–AcOH to 2-nitro-*p*-toluic acid and reduced by Zn dust and AcOH to 2 : 6-*dibromo*-3 : 3′-*diamino*-4 : 4′-*ditolyl*, m.p. 174—175°, which is resolved by *d*-camphorsulphonic acid to the d-*amine*, m.p. 174—175° (probably racemisation occurs before melting), $[\alpha]_D^{23}$ about +0·78° in $COMe_2$ (slowly racemises in solution; half-life period, P= 70·2 min.) (d-*camphorsulphonate*, m.p. 170—180°, $[\alpha]_D^{27}$ about +16° ⟶ about +0·06° in EtOH; P= about 1230 min.), and impure l-*amine* (impure d-*camphorsulphonate*, $[\alpha]_D^{20}$ −15·5° ⟶ $[\alpha]_D^{25}$ −6·5° in MeOH in 50 hr.). R. S. C.

Course of the reaction between magnesium organic compounds and hydroxyazo derivatives. A. Taurinš (Acta Univ. Latviensis, Kim. Fak. Serija, 1934, 2, 321—338).—Mg alkyl halides afford cryst. ppts. with azophenols; the following such *compounds* are described: $X,PhN{:}N{\cdot}C_6H_4{\cdot}OH,2Et_2O$ (I) (X=$CH_2Ph{\cdot}MgCl$, MgEtBr, MgPhBr, MgMeI, MgPhI), $2X,PhN{:}N{\cdot}C_{10}H_6{\cdot}OH(\alpha),n Et_2O$ (II), $X,OH{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH,n Et_2O$. (I) with H_2O regenerates the parent azo-compound; it is concluded that it is not an intermediate in the formation of the hydrazo-compound. Similar *compounds*, $MgPh_2,2PhN{:}N{\cdot}C_6H_4{\cdot}OH,n Et_2O$ (III) and $MgPh_2,PhN{:}N{\cdot}C_{10}H_6{\cdot}OH(\alpha),n Et_2O$ (IV) are obtained with $MgPh_2$, as also with Mg halides, which afford the *compounds* $2MgBr_2,3PhN{:}N{\cdot}C_6H_4{\cdot}OH$, $MgI_2,2PhN{:}N{\cdot}C_6H_4{\cdot}OH$ and $2MgBr_2,3PhN{:}N{\cdot}C_{10}H_6{\cdot}OH(\alpha)$. (I) may be obtained using instead of MgRHal a mixture of MgR_2 and $MgHal_2$. (III) with $MgHal_2$ affords (I), and (IV) similarly yields (II). $BeCl_2$ can replace $MgHal_2$ in these reactions. Ch. Abs. (*r*)

Preparation of hydrazobenzene. C. L. Tseng and F. M. Fan (Sci. Quart. Nat. Univ. Peking, 1935, 5, 350—357).—With Zn dust, < the stoicheiometric proportion of NaOH is required to reduce $PhNO_2$ to $(\cdot NHPh)_2$ (I). 80% of the theoretical yield of (I) was obtained by adding, with shaking, during 30 min., Zn dust (40 g.) to a mixture of NaOH (5·5 g.), H_2O (40 c.c.), $PhNO_2$ (20 g.), and 95% EtOH (80 c.c.) at 80—85° under a reflux. The reaction was completed at 87—90°, and 50% aq. EtOH (180 c.c.) was added before filtering at the b.p. J. G. A. G.

***m*-Nitrobenzohydrazides, 2 : 4-dinitrophenylhydrazones; separation of hydrazones by adsorption.** H. H. Strain (J. Amer. Chem. Soc., 1935, 57, 758—761).—Hydrazones may be purified and mixtures thereof often separated by adsorption on various neutral substances. The following are described: (*a*) m-*nitrobenzhydrazides* of $COMe_2$, m.p. 147·5—149°, COMePh, m.p. 190—191°, CH_2Ac_2, m.p. 119—121°, acraldehyde, m.p. 169·5—171·5°, *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$, m.p. 194·5—196°, benzil, m.p. 232·5—235·5°, $Pr^{\alpha}CHO$, m.p. 135·5—137°, carvone, m.p. 162—163°, $CHPh{:}CH{\cdot}CHO$, m.p. 206—207·5°, citral (commercial) (I), m.p. 100—101°, crotonaldehyde, m.p. 172·5—173·5°, β-*cyclo*citral (II), m.p. 184·5°, *cyclo*hexanone, m.p. 140·5—141·5°, *cyclo*pentanone (III), m.p. 148·5—149·5°, Ac_2 (dihydrazone) (IV), m.p. 320—321°, dicarvelone (mixture; dihydrazone), m.p. 95—100°, *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ (V), +0·5$PhNO_2$, m.p. 219·5—221°, furfuraldehyde, m.p. 195—197°, glyoxal (dihydrazone) (VI), m.p. 339·5—340·5°, $C_6H_{13}{\cdot}CHO$, m.p. 108·5—110·5°, α- (VII), m.p. 149·5—150·5°, and β-ionone (VIII), m.p. 161—162·5°, $Pr^{\beta}CHO$, m.p. 141·5—142·5°, lævulic acid (IX), m.p. 181·5—182·5°, lævulaldehyde (dihydrazone) (X), m.p. 155·5—156°, menthone, m.p. 105—107°, mesityl oxide, m.p. 120—140°, 2-methyl*cyclo*hexanone (XI), m.p. 115·5—118°, methylheptenone, m.p. 99—100°, *p*-$C_6H_4Me{\cdot}COMe$, m.p. 193—194°, *m*-$NO_2{\cdot}C_6H_4{\cdot}CHO$, m.p. 253—255°, nonaldehyde, m.p. 87°, piperonal, m.p. 229—230·5°, EtCHO, m.p. 156·5—158·5°, $AcCO_2H$ (XII), m.p. 185·5—186·5°, AcCHO (dihydrazone) (XIII), m.p. 288·5°, thujone (XIV), m.p. 156—156·3°, *p*-$C_6H_4Me{\cdot}CHO$ (XV), m.p. 189—190·5°, 2 : 4 : 6-$(NO_2)_3C_6H_2{\cdot}CHO$, m.p. 238—239° (decomp.), vanillin, m.p. 213—215°, and veratraldehyde (XVI), m.p. 225·5—227·5°; (*b*) 2 : 4-*dinitrophenylhydrazones* of MeCHO, m.p. 163·5—164·5°, $CH_2Ac{\cdot}CO_2Et$, m.p. 96°, acetol, m.p. 127·5—129·5°, $CO_2H{\cdot}[CH_2]_7{\cdot}CHO$, m.p. 114—115°, (I), m.p. 99—115°, (II), m.p. 171—172°, (III), m.p. 145·5—146·5°, (IV), m.p. 314—315°, (V), m.p. 324·5—326° (decomp.), geronic acid, m.p. 135·5—137°, (VI), m.p. 326—328°, (VII), m.p. 147·5—149·5°, (VIII), m.p. 128—129°, *iso*geronic acid, m.p. 140—141°, (IX), m.p. 206°, Et, m.p. 101—102°, Me, m.p. 141·5—142·5°, Pr^{α}, m.p. 67—68°, and Pr^{β} lævulate, m.p. 88—89°, (X), m.p. 235·5—236·5°, (XI), m.p. 135·5—137°, $C_8H_{17}{\cdot}CHO$, m.p. 100°, (XII), m.p. 218°, Et, m.p. 154·5—155°, Me, m.p. 186·5—187·5°, Pr^{α}, m.p. 119—120°, and Pr^{β} pyruvate, m.p. 160·5—161·5°, (XIII), m.p. 299—300°, (XIV), m.p. 106—107·5°, (XV), m.p. 232·5—234·5°, and (XVI), m.p. 261—263°. *m*-Nitrobenzohydrazide is stable in H_2O, but in acid slowly gives NN′-*bis*-m-*nitrobenzohydrazide*, m.p. 240—242°. 2 : 4-$(NO_2)_2C_6H_4{\cdot}NH{\cdot}NH_2$ is decomposed by alkalis, giving with hot Na_2CO_3 a *substance*, exploding at 190—192°, and with hot 6*N*-NaOH a *substance*, m.p. 145·5—147·5°; with a little AcOH in H_2SO_4–EtOH it gives the *Ac* derivative, m.p. 201°. Pinacol gives the 2 : 4-dinitrophenylhydrazone of pinacone. M.p. are corr. R. S. C.

Character of the diazonium group. Preparation of disazo-dyes from *m*-phenylenediamine. H. A. J. Schoutissen (Rec. trav. chim., 1935, 54, 381—386).—Tetrazotised *m*-$C_6H_4(NH_2)_2$ in conc. HCl couples with one mol. of a phenol, including β-$C_{10}H_7{\cdot}OH$ (I), PhOH, 2 : 6-$OH{\cdot}C_{10}H_6{\cdot}SO_3Na$, 1 : 8 : 3 : 6-$NH_2{\cdot}C_{10}H_4(OH)(SO_3H)_2$, α-$C_{10}H_7{\cdot}OH$, *m*-$C_6H_4(OH)_2$, and *o*-cresol, to give cryst. *azo-diazo*-compounds which couple with phenols in alkaline solution to give *benzene*-1 : 3-*disazo*-β-*naphthol*, m.p. 251°, -1 : 3-*disazophenol*, m.p. 216°, -1-*azophenol*-3-*azo*-β-*naphthol*-, m.p. 230°, 1-*azo*-β-*naphthol*-3-*azo*-β-*naphthol*-6′-*sulphonic acid* (*Na* salt), and -1-*azo*-β-*naphthol*-3-*azo*-(1′ : 8′-*aminonaphthol*-3′ : 6′-*disulphonic acid*). Coupling with *p*-cresol or PhOMe does not give cryst. compounds. (I) with

KI in 2*N*-H_2SO_4 gives m-*iodobenzeneazo*-β-*naphthol*, m.p. 185—186°. The coupling in acid solution is attributed to the influence of the strongly negative character of a diazonium group on a diazo-group, the tetrazotised compound being given the structure N:N(X)·C_6H_4·N:NX in acid solution. F. R. G.

Thermal decomposition of γ-phenoxy-αγ-oxido-β-methylbutyric acid. B. Rothstein (Bull. Soc. chim., 1935, [v], **2**, 653—656).—Condensation of $CH_2Cl·CO_2Et$ with $CH_2Ac·OPh$ in presence of NaOEt at < 0° affords a 73% yield of *Et γ-phenoxy-αγ-oxido-β-methylbutyrate*, b.p. 175—178°/15 mm., hydrolysed by KOH–EtOH to the corresponding *acid* (I), m.p. 73·5—74° (block) (*K* salt). Thermal decomp. of (I) at 160—180°/13 mm. occurs thus: (I) ⟶ CO_2 + [OPh·CH_2·CHMe·CHO] ⟶ PhOH + CH_2:CMe·CHO. J. W. B.

Organic reactions with boron fluoride. IX. Alkylation of phenol with alcohols. F. J. Sowa, G. F. Hennion, and J. A. Nieuwland (J. Amer. Chem. Soc., 1935, **57**, 709—711; cf. this vol., 195).—PhOH–BF_3 (21%) with MeOH or EtOH at 170° (3 hr.) gives PhOMe (58%) or PhOEt (17%), respectively. Pr$^{\alpha}$OH and Pr$^{\beta}$OH give 2 : 4-$C_6H_3Pr^{\beta}_2$·OPr$^{\beta}$ (11 and 13%), *o*- (28 and 32%) and *p*-$C_6H_4Pr^{\beta}$·OH (20 and 16%, respectively). Reaction thus occurs by preliminary dehydration to C_3H_6 and not by direct condensation. R. S. C.

Sulphonating action of sulphuric acid in aqueous and acetic solutions.—See this vol., 710.

Molecular compounds of phenols. G. T. Morgan and A. E. J. Pettet (J.S.C.I., 1935, **54**, 22—24T).—By f.-p. determinations of mixtures of the two components, the following mol. *compounds* of phenol homologues were shown to be formed (molecular proportions and m.p. in parentheses): (*a*) with cineole: m-2- (1 : 1; m.p. 12·0°), m-4- (2 mols. xylenol, m.p. 37·9°), m-5- (1 : 1, m.p. −0·1), and p-*xylenol* (1 : 1, m.p. 26·8°); o- (1 : 1, m.p. 4·4°) and p-*ethylphenol* (1 : 1, m.p. −4·1°); 2-*methyl*-4- (2 mols. phenol, m.p. 4·1°) and 2-*methyl*-6-*ethylphenol* (1 : 1, m.p. −23·1°). (*b*) With *m*-5-xylidine: *phenol* (1 : 1, m.p. 9·2°); o- (1 : 1, m.p. 48·3°), m- (1 : 1, m.p. 4·9°; 2 mols. cresol, m.p. 10·1°), and p-*cresol* (2 mols. cresol, m.p. 20·2°); m-2- (1 : 1, m.p. 21·9°), m-4- (1 : 1, m.p. 36·3°), m-5- (1 : 1, m.p. 36·3°), and p-*xylenol* (1 : 1, m.p. 65·1°); o- (1 : 1, m.p. 30·0°) and p-*ethylphenol* (2 mols. phenol, m.p. 13·9°); 2- (1 : 1, m.p. 27·4°) and 3-*methyl*-4-*ethylphenol* (1 : 1, m.p. 23·5°; 2 mols. phenol m.p. 22·9°); 3-*methyl*-6- (1 : 1, m.p. 43·1°) and 4-*methyl*-2-*ethylphenol* (1 : 1, m.p. 33·0°). (*c*) With 3 : 5 : 3′ : 5′-dixylylamine: o- (1 : 1, m.p. 16·1°), m- (2 mols. base, m.p. 31·5°), and p-*cresol* (1 : 1, m.p. 21·7°). Indications of metastable compounds were obtained between *o*-4-xylenol–cineole (2 : 1) and *o*-4-xylenol–*m*-5-xylidine (2 : 1). No combination could be detected between cineole and 3-methyl-4-, 3-methyl-6-, or 4-methyl-3-ethylphenol.

Synthesis of carvacrol. D. Gardner, M. Procofief, G. Jusov, and M. L. Caselli (Compt. rend., 1935, **200**, 1114—1115).—Pure carvacrol, b.p. 236°, m.p. 0·5°, is obtained from *p*-cymene through the NO_2-, NH_2-, and diazo-compounds. It is also obtained by the interaction of *o*-cresol and Pr$^{\beta}$OH in presence of P_2O_5. It can be converted into a carboxylic acid by CO_2 without pressure. F. N. W.

4-Chloro-2-nitro- and -2-amino-phenol. M. Mottier (Arch. Sci. phys. nat., 1934, [v], **16**, 301—303).—The prep. of these substances from *p*-$C_6H_4Cl·OH$ is modified to give 65 and 53·6%, yields, m.p. 86—87° and 137·5—138·5°, respectively. R. S. C.

Methyl-*p*-aminophenol. N. I. Kirillov (Photo-Kino Ind., 1933, 70—80).—The prep. of *p*-methylaminophenol by condensation of *p*-aminophenol (I) and PhCHO and by methylation of (I) hydrochloride with MeOH is described, the first process being used technically. Ch. Abs. (*r*)

Preparation of phenacetin from phenol in laboratory practice. S. Vlăduță (Curierul Farm., 1934, **4**, No. 5, 16—20; No. 6, 1—10; No. 7, 1—17; Chem. Zentr., 1934, ii, 3611).—The available methods are discussed. The best yield of *p*-nitrophenol (I) is obtained from PhOH and HNO_3 (*d* 1·09) at 15—25°. Reduction of (I) is best carried out with Zn dust or $NaHSO_3$. H. N. R.

Preparation of 1-alkyl-β-naphthols. K. Dziewoński and C. Dragan [with C. Marchovna] (Bull. Acad. Polonaise, 1934, **A**, 398—401).—β-$C_{10}H_7$·OH, dry NPhMe$_2$ or NPhEt$_2$, and a trace of β-$C_{10}H_7$·ONa at 300° (autoclave) give 55—60% yields of 1-*methyl*-, m.p. 101° (*picrate*, m.p. 163—164°), and 1-*ethyl*-β-*naphthol*, m.p. 105° (*Bz* derivative, m.p. 75°), with a little alkali-insol. substance (not an *O*-alkyl compound). R. S. C.

Action of hydroxylamine on certain naphthalene derivatives. S. V. Bogdanov and I. I. Levkoev (J. Gen. Chem. Russ., 1934, **4**, 1353—1358; cf. A., 1933, 389).—NH_4 2-nitroso-α-naphthol-4-sulphonate is obtained from aq. NH_2OH,HCl and 1-amino-β-, 2-amino-α-, or 1-nitroso-β-naphthol-4-sulphonic acid; the corresponding 5-sulphonate is obtained analogously from 2-amino-α-naphthol- or 1 : 2-naphthylenediamine-5-sulphonic acid. The mechanism of the reactions involved is discussed. R. T.

Substituted phenyldihydroresorcinols. L. E. Hinkel, E. E. Ayling, and J. F. J. Dippy (J.C.S., 1935, 539—540).—*o*-Chlorobenzylideneacetone (modified prep.), m.p. 24·5° (lit., an oil), b.p. 160—163°/17 mm., $CH_2(CO_2Et)_2$, and NaOEt at 100° give 5-*o*-*chlorophenyldihydroresorcinol*, m.p. 149° (decomp.). The 5-*o*-, m.p. 145°, and -p-*OMe*-compounds, m.p. 175° (decomp.), are similarly prepared. R. S. C.

Catalytic reduction of substituted ω-nitrostyrenes. B. Reichert and W. Koch (Arch. Pharm., 1935, **273**, 265—274).—Good yields (90%) of $CH_2Ar·CH$:NOH are obtained by reduction of CHAr:CH·NO_2 with Pd–C–H_2 in C_5H_5N, and thus are obtained β-*o*-, -*p*-, -2 : 4- (I), and -3 : 4-di-methoxy- and -3 : 4-methylenedioxy-phenylacetaldoxime. (I) is converted by Ac_2O into 2 : 4-*dimethoxyphenylacetonitrile*, m.p. 75°, hydrolysed to the known acid. Reduction of (I) in $H_2C_2O_4$–EtOH with H_2–PtO_2 at room temp. affords the *oxalate* +0·5H_2O (II), m.p. 155°, of β-2 : 4-dimethoxyphenylethylamine (*Bz* derivative, m.p. 115°), and the *oxalate*, m.p.

170°, of *di*-(β-2 : 4-*dimethoxyphenylethyl*)*hydroxylamine*, m.p. 128° (*hydrochloride*, m.p. 151°), reduced (Sn–HCl–aq.EtOH) to di-(β-2 : 4-dimethoxyphenylethyl)-amine, isolated as its *H oxalate*, m.p. 203° [also by direct reduction of (I)]. With $NaNO_2$ (II) gives β-2 : 4-*dimethoxyphenylethyl alcohol*, m.p. 67°. By similar methods are obtained the *H oxalate*, m.p. 180°, of β-*o*-anisylethylamine, and the *oxalate*, m.p. 137°, of di-(β-*o*-anisylethyl)hydroxylamine.

J. W. B.

Highly-polymerised compounds. CIX. Viscosity of polyphenyl ethers. H. Staudinger and F. Staiger (Annalen, 1935, **517**, 67—72).—Determinations of the viscosity of polyphenyl ethers in CCl_4 and C_6H_6 at 20° and 60° and in $CHCl_3$ at 20°, 40°, and 60° show that $\eta_{sp.}$ varies with temp. in the manner observed with other compounds of low mol. wt. In C_6H_6 and $CHCl_3$ the increments for a Ph group are greater for the simple than for the more complex products, whereas in CCl_4 they remain const. In CCl_4 and in C_6H_6 for the substances rich in Ph the increment is $3{\cdot}0\times10^{-3}$, which is approx. the val. found for simple aromatic compounds. The viscosity increases regularly with successive addition of OPh to the ether mol. The following compounds have been employed : Ph_2O; quinol Ph_2 ether (I), m.p. 77°; *pp'*-diphenoxydiphenyl ether (II) m.p. 110°; *quinol* pp'-*diphenoxydiphenyl ether*, m.p. 151°, prep. by converting (I) into the corresponding Br_2-compound, m.p. 131°, which is treated according to Allmann *et al.* (A., 1907, i, 35); pp'-*diphenoxydiphenoxydiphenyl ether* ($OPh{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_4)_2O$, m.p. 173°, obtained similarly from the Br_2-compound, m.p. 162°, of (II). Quinol is quantitatively converted by H_2 at 200°/150 atm. in EtOH in presence of Ni into *cis*-quinitol, m.p. 103—104°. The corresponding dibromide is transformed by NaOPh in PhOH containing Cu powder into *Ph* Δ^3-cyclo*hexenyl ether* (III) and by *cyclo*hexanol into cyclo*hexyl* Δ^3-cyclo*hexenyl ether* (IV). In 1·4% solution in CCl_4, Ph_2O, CH_2Ph_2, (III), and (IV) have the same $\eta_{sp.}$ within the limits of experimental error; measurements are recorded at 20°, 40°, and 60°. H. W.

Configuration of alicyclic alcohols. II. Configuration and cryscopic behaviour of alcohols. W. Hückel, K. Kumetat, and W. Preuss [with, in part, Severin, J. Yantschulevitsch, B. Schwerin, Müller-Lotz, and (Frln.) H. Kasczemek] (Annalen, 1935, **517**, 229—244; cf. this vol., 340).—The *cis*-forms of alicyclic alcohols, *e.g.*, the 2-alkyl*cyclo*hexanols, have usually higher *d* and n_D, but lower $[M]_D$ and η, than the *trans*-forms. The former are also less associated (cryoscopic determination) in solvents, particularly in *cyclo*hexane and C_6H_6, and the apparent mol. wt. increases more slowly with increasing concn. This is probably due to steric "protection" of the OH, since α-decalols are less associated than their β-isomerides, but more than the 9-decalols. This explanation is in line with the lower rate of hydrolysis of esters of the *cis*- and α-isomerides. The 9-decalols, m.p. 54° and 65°, are thus shown to be the *trans*- and *cis*-forms, respectively. Other factors, at present not understood, are, however, also concerned; thus, *e.g.*, *trans*-2-*cyclo*hexyl-*cyclo*hexanol shows a much more rapid increase in mol. wt. with concn. than the *cis*-isomeride (curves cross at 0·4 mol.-%) or than *tert.*-1-*cyclo*hexyl*cyclo*hexanol (curves cross at 0·8 mol.-%) in *cyclo*hexanol. The following data appear to be new : *cis*-α-hydrindanol (prep. by Na–EtOH), an oil (H phthalate, m.p. 140°), and an isomeride [prep. by catalytic hydrogenation (*A*)], m.p. 18° (H phthalate, m.p. 127°) : *cis*-4-hydroxyhydrindane [prep. by (*A*)], dimorphic (H phthalate, m.p. 134°); 1-*ethyl*cyclo*pentan*-1-*ol* (from *cyclo*pentanone and MgEtBr), m.p. —8°, b.p. 155—157°/760 mm., 61°/17 mm.

R. S. C.

Products of the transformation of acetylenic carbinols. Constitution of the compounds derived from phenylethylmethylethinylcarbinol. H. Rupe and H. Werdenberg (Helv. Chim. Acta, 1935, **18**, 542—546).—The ketone, b.p. 140—140·5°/9 mm. (semicarbazone, m.p. 182°), obtained by Rupe *et al.* (A., 1931, 1050) by the action of HCO_2H on $CH_2Ph{\cdot}CH_2{\cdot}CMe(OH){\cdot}C{\equiv}CH$ is converted by O_2 in CCl_4 into $CH_2Ph{\cdot}COMe$, AcOH, and BzOH and is therefore α-*phenyl*-β-*methyl*-Δ^{β}-*penten*-δ-*one*. The aldehyde obtained simultaneously (*loc. cit.*) when ozonised gives $CH_2Ph{\cdot}CH_2{\cdot}COMe$ and HCO_2H and hence is δ-*phenyl*-β-*methyl*-Δ^{α}-*pentenal* (I). (I) polymerises and resinifies very readily. It condenses with $COMe_2$ to a product (*semicarbazone* $C_{16}H_{21}ON_3$, m.p. 164°). H. W.

[Law of periodicity and the conjugated system.] P. Petrenko-Kritschenko (Ber., 1935, **68**, [*B*], 618; cf. A., 1934, 1000).—A reply to Hantzsch *et al.* (this vol., 487). H. W.

Condensation of cholesteryl chloroformate with alcohols and phenols. E. Schadendorff and A. Verdino (Monatsh., 1934, **65**, 338—347).—By condensation in Et_2O or C_6H_6 of cholesteryl chloroformate with the appropriate OH-compound in presence of C_5H_5N, $NHPh_2$, or Na, *dicholesteryl carbonate*, m.p. 176°, and the following are obtained : *Et*, m.p. 83°, *Ph*, m.p. 123°; m-, m.p. 116°, and p-*tolyl*, m.p. 122°, sinters 115°, m-, m.p. 134°, and p-*nitrophenyl*, m.p. 162°, o-*carbomethoxyphenyl*, m.p. 130—131°, o-*carbophenoxyphenyl*, m.p. 150—151°, 2 : 4 : 6-*tribromophenyl*, m.p. 111°, p-*aldehydophenyl*, m.p. 129°, α-, m.p. 166°, and β-*naphthyl*, m.p. 173°, sinters 164°, 4-*benzeneazophenyl*, m.p. 166°, p-(*cholesterylcarbamyl*)*phenyl*, m.p. 215°, *cholesteryl-carbonates*; o-, m.p. 160—161°, m-, m.p. 216°, sinters, 213°, and p-, m.p. 234°, sinters 215°, -*phenylene dicholesteryl dicarbonate*; *pyrogallol*, m.p. 213°, sinters 180°, and *phloroglucinol*, m.p. 143°, *tricholesteryl tricarbonate*. Many of the esters form liquid crystals.

F. R. G.

Condensation products from alcohols and phenols.—See B., 1935, 443.

***cyclo*Hexadienes.** N. D. Zelinski, J. I. Denisenko, and M. S. Eventova (Compt. rend. Acad. Sci. U.R.S.S., 1935, **1**, 313—320).—*cis-cyclo*Hexane-1 : 4-diol and freshly heated $MgSO_4$ on warming (4—5 hr.) afford $\Delta^{1:3}$- (I), b.p. 80·5—80·7°/752 mm. (cf. lit.), and $\Delta^{1:4}$- (II), b.p. 88·8—89·2°/758 mm. (cf. lit.), -*cyclo*hexadiene in the proportion 8 : 1. CO_2 is passed through the mixture during the progress of the re-

action and removes the products, which are then condensed. When $KHSO_4$ is used (I) and (II) are formed in the proportion 1 : 2. (I) and (II) are separated by fractional distillation from BaO. With EtOH–H_2SO_4 (I) gives a dark blue-violet coloration, whilst (II) gives a pink and faintly blue-violet coloration. Oxidation of (I) with 1% aq. $KMnO_4$ below 0° gives 1 : 2 : 3 : 4-*tetrahydroxy*cyclo*hexane*, m.p. 153—154°, which has a sweet taste. Similarly (II) affords 1 : 2 : 4 : 5-tetrahydroxy*cyclo*hexane, m.p. 239—240° (cf. A., 1931, 945). H. G. M.

Constitution of Δ^3-*cyclo*hexene-1 : 2-diol; some αβ-derivatives of adipic acid. P. Bedos and A. Ruyer (Compt. rend., 1935, **200**, 944—946).—The Δ^3-structure for this diol (cf. A., 1933, 500) is confirmed by oxidation (Thiele method) of its dibromide to αβ-*dibromoadipic acid*, m.p. 143°, which is hydrolysed to the (*OH*)$_2$-*acid* (not isolated), and reduced to a Δ^1-*butylene*-αδ-*dicarboxylic acid*, (I), m.p. 210°, stereoisomeric with $\Delta^{\alpha\beta}$-dihydromuconic acid. (I) is reduced quantitatively to adipic acid, and oxidised to oxalic and succinic acids. E. W. W.

Condensation of 2 : 6-dimethylol-*p*-cresol with esters of higher fatty acids. T. P. Hilditch and C. J. Smith (J.S.C.I., 1935, **54**, 111—115T).—When 2 : 6-dimethylol-*p*-cresol (I) and a simple (Me) ester of a saturated (palmitic) or monoethylenic (oleic) acid are heated together at 240°, a certain amount of displacement of the Me by the phenolic alcohol group takes place, but no other action of condensation between the phenolic alcohol and the aliphatic ester. With polyethenoid esters, condensation at the unsaturated centres proceeds to a considerable extent, especially in the case of elæostearic esters. No condensation occurs when (I) and aliphatic paraffins are heated together at 240°. The interaction with linseed oil (II) or tung oil (III) is determined by the nature of the component fatty acids of these oils. In the case of (III) it proceeds far towards completion. Boiled (II) appears to interact more readily than raw (II). The mixed linoleo-linoleno-glycerides of (II) enter most readily into condensation, and saturated or oleic radicals do not commence to pass into the petrol-insol. resin product until condensation has taken place to a marked extent.

Inositolphosphoric acid compounds. III. Compounds of ferric inositolphosphate with the sodium and potassium salts of certain hydroxy-acids. S. Otolski (Rocz. Chem., 1935, **15**, 99—104).—Fe_4 inositolphosphate yields a 1 : 3-*compound* (+15H_2O) with $(NH_4)_3$ citrate, a 1 : 5-*compound* (+10H_2O) with K_3 citrate, a 1 : 6-*compound* (+10H_2O) with $(NH_4)_2$ malate, and a 1 : 8-*compound* (+16H_2O) with K_2 malate. The salts are readily sol. in H_2O. R. T.

Bromination of substances containing two aromatic nuclei. I. Bromination of tolyl and nitrophenyl benzoates. G. V. Jadhav and Y. I. Rangwala (J. Indian Chem. Soc., 1935, **12**, 89—92).—With Br and HNO_3 (*d* 1·45) on a water-bath the Bz derivatives of *o*-, *m*-, and *p*-cresol afford, respectively, 4-bromo-*o*-, 4-bromo-*m*-, and 2-*bromo*-p-*tolyl benzoate*, m.p. < 0°, identical with synthetic specimens. On similar treatment of *o*-, *m*-, and *p*-nitrophenyl benzoate, Br enters the benzoic nucleus to give, respectively, o-, m.p. 105°, m-, m.p. 132°, and p-*nitrophenyl* m-*bromobenzoate*, m.p. 122°, converted by further bromination into o-, m.p. 132°, m-, m.p. 165°, and p-*nitrophenyl* 2 : 5-*dibromobenzoate*, m.p. 183—184°, respectively. J. W. B.

5-Bromo-2 : 4-dimethylbenzoic acid. Nuclear halogenation with alkaline hypohalite solution. C. H. Fisher and M. Grant (J. Amer. Chem. Soc., 1935, **57**, 718—719).—NaOBr gives good yields of the derived benzoic acid from $CH_2Ph{\cdot}CO_2H$, benzoin, deoxybenzoin, CH_2PhCl, CH_2PhBr, *o*-$C_6H_4Me{\cdot}CH_2Cl$, *o*-$C_6H_4Me{\cdot}CH_2Br$, and *m*-$C_6H_4Ac{\cdot}NO_2$. Since the speed of conversion of the benzyl halides into benzoic acids is approx. ∝ the rate of hydrolysis of the former, it is believed that hydrolysis of the halomethyl group precedes oxidation. Two Me groups, however, cause halogenation of the Ph nucleus. Thus, 5-bromo-2 : 4-dimethylbenzoic acid (I), m.p. 180—181° (amide, m.p. 197·5—198·5°), also obtained from 5-*bromo*-2 : 4-*dimethylbenzonitrile*, m.p. 88—89°, is formed from 2 : 4-dimethyl-acetophenone (II) (cf. Perkin *et al.*, A., 1926, 64), -phenacyl chloride, -benzoic or -mandelic acid. 5-Bromo-ψ-cumene and HNO_3 give a different acid, m.p. 172—173°, previously considered to be (I). β-*iso*Durylic acid gives (NaOBr) 3-bromo-2 : 4 : 6-trimethylbenzoic acid, and (II) and NaOCl give an acid, m.p. 164—165·6°, probably 5-chloro-2 : 4-dimethylbenzoic acid. R. S. C.

Metabolism of norleucine, *iso*leucine, and valine. I. Synthesis of some phenyl derivatives. H. E. Carter (J. Biol. Chem., 1935, **108**, 619—632).—Series of phenylated NH_2-acids and fatty acids were made for the purpose of studying their behaviour in animal metabolism. α-Amino-β-phenylhexoic and -β-*methyl*-γ-*phenylbutyric acid*, m.p. 235—245°, were synthesised by the method of Braun (A., 1912, i, 265) modified by replacing Br by NH_2 before decarboxylation. *Et* α-*carbethoxy*-γ-*phenyl*-β-*ethylbutyrate*, b.p. 145—147° (4 mm.), -δ-*phenyl*-β-*methylvalerate*, b.p. 159—161° (2 mm.), α-*carboxy*-γ-*phenyl*-β-*methylbutyric*, m.p. 143—145°, -γ-*phenyl*-β-*ethylbutyric*, m.p. 150—151°, -δ-*phenyl*-β-*methylvaleric*, m.p. 83—84°, α-*bromo*-α-*carboxy*-γ-*phenyl*-β-*methylbutyric*, m.p. 153—154°, -γ-*phenyl*-β-*ethylbutyric*, m.p. 152—153°, -δ-*phenyl*-β-*methylvaleric*, m.p. 118—119°, α-*amino*-α-*carboxy*-γ-*phenyl*-β-*methylbutyric*, m.p. 255—265°, -γ-*phenyl*-β-*ethylbutyric*, m.p. 240—245°, and -δ-*phenyl*-β-*methylvaleric acid*, m.p. 225—230°, are described. α-*Amino*-δ-*phenyl*-β-*benzylvaleric acid*, m.p. 240—250° (I), is prepared by treatment of dimethylcinnamylidenemalonate with $CH_2Ph{\cdot}MgCl$ in Et_2O and hydrolysis, giving α-*carboxy*-γ-*styryl*-β-*benzylbutyric acid*, m.p. 177—179° (II), which with PBr_3 gives α-*bromo*-α-*carboxy*-δ-*phenyl*-β-*benzylvaleric acid*, m.p. 150—152°; this with aq. NH_3 gives α-*amino*-α-*carboxy*-δ-*phenyl*-β-*benzylvaleric acid*, m.p. 245—255°; on decarboxylation (I) is obtained. From (II) γ-*styryl*-β-*benzylbutyric*, b.p. 215—217°/1 mm., and δ-*phenyl*-β-*benzylvaleric acid*, b.p. 210—215°/3 mm., are obtained. α-*Amino*-γ-*phenyl*-β-*benzylbutyric acid*, m.p. 260—270° (III), is prepared from ethoxymethylenemalonic ester by treatment with $CH_2Ph{\cdot}MgCl$, giving *Et* α-*carbethoxy*-γ-*phenyl*-

β-*benzylbutyrate*, b.p. 188—203°/3 mm., which on hydrolysis gives α-*carboxy*-γ-*phenyl*-β-*benzylbutyric*, m.p. 153—155° (IV), and γ-*phenyl*-β-*benzylbutyric acid*, b.p. 195—200°/2 mm. Treatment of (IV) with PBr_3 gives α-*bromo*-α-*carboxy*-γ-*phenyl*-β-*benzylbutyric acid*, m.p. 166—168°, which with aq. NH_3 gives α-*amino*-α-*carboxy*-γ-*phenyl*-β-*benzylbutyric acid*, m.p. 265—275°, which on decarboxylation gives (III). β-*Bromo*-α-*phenylbutane*, b.p. 98—99°/1 mm., is made by reduction of $CH_2Ph{\cdot}COEt$ to the carbinol and treatment with PBr_3 at −5°. H. D.

Reactions of aminobenzoic acids with cadmium and zinc salts.—See this vol., 719.

Syntheses of isomeric phenylbutadienecarboxylic acids. II. Synthesis of *iso*chavicic acid. H. Lohaus and H. Gall (Annalen, 1935, **517**, 278—289; cf. A., 1934, 1348).—*iso*Chavicic acid (I) is synthesised in poor yield, thus completing the series of isomeric δ-phenylbutadiene-α-carboxylic acids. Here, as in the diphenylbutadiene and dibromomuconic ester series, the order of increasing stability, as judged by the m.p., is *trans-trans* > *cis-cis* > *cis-trans*. Therefore, (I), and not chavicic acid as assumed by Ott (A., 1922, i, 1026), occurs as piperide in pepper. Piperonal and MeCHO in NaOH–EtOH at 8—10° give a little piperinaldehyde, b.p. 185—195°/0·05 mm., m.p. 108° (lit. 89—90°) [phenylhydrazone, m.p. 158—159° (lit. 190—192°); stereoisomeric *oximes*, m.p. 171° and 195°], and piperonylacraldehyde (II) (30% yield), b.p. 170—185°/0·05 mm.; (II) with cold Br–AcOH gives α-*bromo*-cis-*piperonylacraldehyde* (III), m.p. 104° (*oxime*, m.p. 182°), and some αβ-*dibromo*-compound, m.p. 131° (*oxime*, m.p. 205°; oxidised by $KMnO_4$ to 6-bromopiperonylic acid, m.p. 203°). (II), $CH_2(CO_2Me)_2$, and a few drops of piperidine (IV) in MeOH give slowly *Me*$_2$ 3 : 4-*methylenedioxy*-γ-cis-*cinnamylidenemalonate*, m.p. 111°, and (III) gives similarly the γ-*Br*-ester, m.p. 126°. (II), $CN{\cdot}CH_2{\cdot}CO_2Me$, and a little (IV) in MeOH give rapidly a little Me α-cyano-3 : 4-methylenedioxycinnamate, m.p. 169° [derived from residual piperonal in (II)], and *Me* 3 : 4-*methylenedioxycinnamylidenecyanoacetate* (75% yield), m.p. 189° (*Et* ester, similarly obtained from $CN{\cdot}CH_2{\cdot}CO_2Et$, m.p. 130°); (III) gives similarly a little piperidine hydrobromide by loss of HBr, but mostly *Me* γ-*bromo*-α-*cyano*-3 : 4-*methylenedioxy*-γ-cis-*cinnamylideneacetate*, m.p. 167° (also obtained in very poor yield by adding Br to Me α-cyano-3 : 4-methylenedioxy-γ-*trans*-cinnamylideneacetate and removing HBr by KOAc–MeOH), which with Zn dust in 90% MeOH gives a bimol., amorphous *substance*, $C_{28}H_{20}O_8N_2$, m.p. 98—102° after sintering; the product previously obtained similarly from the corresponding CH_2O_2-free ester is also bimol. (II) and NaOAc in hot Ac_2O give γ-*bromo*iso*chavicic acid* (V), m.p. 216° (*Me* ester, m.p. 120—121°), also obtained in poor yield, with a *substance*, m.p. 152°, from (III) and $CH_2(CO_2H)_2$ in C_5H_5N at about 140°. (V) and Zn dust in hot 90% MeOH or EtOH give much piperic acid (VI) (with or without its ester) and a little 3 : 4-*methylenedioxy*-α-trans-γ-cis-δ-*phenylbutadiene*-α-*carboxylic acid* (I), m.p. 138—139°, hydrogenated (Pd-black) in MeOH to $CH_2Ph{\cdot}[CH_2]_3{\cdot}CO_2H$. The configuration of the γ-linking of (I) follows from the non-identity of (I) with piperic or *iso*piperic acid, that of the α-linking from the fact that the *trans*-compound (VI) accompanied (I) and that inversion during hydrogenation is improbable. Other configurations cited above follow. R. S. C.

Effect of substituents on formation of chloralides of salicylic acid and its derivatives. R. L. Alimchandani, N. M. Shah, and S. G. Deo (Current Sci., 1935, **3**, 354).—*o*-$OMe{\cdot}C_6H_4{\cdot}CO_2H$ and $CCl_3{\cdot}CHO$ give 2-methoxy-5-βββ-trichloro-α-hydroxyethylbenzoic acid (A., 1934, 1216), but 3- and 5-nitro-6-hydroxybenzoic acid and the corresponding Me ethers fail to react with $CCl_3{\cdot}CHO$. F. N. W.

Action of thionyl chloride on phenylglycollic acid. P. Carré and D. Libermann (Compt. rend., 1935, **200**, 1215—1217).—$SOCl_2$ with $OH{\cdot}CHPh{\cdot}CO_2H$ (I) gives $CHPhCl{\cdot}CO_2H$ (cf. A., 1934, 290; J.C.S., 1911, **99**, 1910) and $CHPhCl_2$ which arises from PhCHO by the decomp. (> 30°) of an anhydro-sulphite (II) (cf. A., 1922, i, 715). In Et_2O at 0° (I) with $SOCl_2$ gives an oil, converted by EtOH into $OH{\cdot}CHPh{\cdot}CO_2Et$ which is formed from (II). $OH{\cdot}CPh_2{\cdot}CO_2H$ is converted into $COPh_2$ probably through an anhydrosulphite (cf. A., 1902, i, 31), since *tert.*-alcohols yield no chlorosulphites. J. L. D.

Preparation of δ-phenyl-β-methyl-*n*-valeraldehyde. H. Rupe, H. Hirschmann, and H. Werdenberg (Helv. Chim. Acta, 1935, **18**, 535—542).—The action of Mg and $HgCl_2$ on $COMe{\cdot}CH_2{\cdot}CH_2Ph$ and $CH_2Br{\cdot}CO_2Et$ in C_6H_6–Et_2O gives *Et* β-*hydroxy*-δ-*phenyl*-β-*methyl*-n-*valerate*, which loses H_2O when distilled in vac. with formation of a mixture (I) of the corresponding unsaturated esters. Hydrolysis of (I) gives a mixture of acids from which δ-*phenyl*-β-*methyl*-γ-*valerolactone*, b.p. 179—181°/11 mm. (*Ca* salt of corresponding OH-acid), is obtained by treatment with 50% H_2SO_4, which does not affect the δ-*phenyl*-β-*methyl*-Δ$^{\alpha}$-n-*pentenoic acid*, b.p. 179°/10 mm. (*Ca* salt). Hydrogenation of (I) (Ni–dil. EtOH) affords *Et* δ-*phenyl*-β-*methyl*-n-*valerate*, b.p. 151—154°/12 mm., reduced by Na and EtOH in light petroleum to ε-*phenyl*-γ-*methyl*-n-*amyl alcohol* (II), b.p. 141—143°/11 mm. Catalytic oxidation of (II) (Ag–asbestos) gives δ-*phenyl*-β-*methyl*-n-*valeraldehyde*, b.p. 142—144°/11 mm. (*semicarbazone*, m.p. 130), which very rapidly polymerises. H. W.

6-Nitroveratraldehyde and hippuric acid. A. Oliverio (Gazzetta, 1935, **65**, 143—152).—The condensation product of veratraldehyde and hippuric acid (I) is hydrolysed, through the cinnamic acid, to the acetic acid, which can be nitrated to 6-*nitro*-3 : 4-*dimethoxyphenylacetic acid* (II), m.p. 207—208°. The product from 6-nitroveratraldehyde and (I), 2-*phenyl*-4-(6′-*nitro*-3′ : 4′-*dimethoxybenzylidene*)-1 : 3 : 5-*oxazolone*, m.p. 227—228°, is similarly hydrolysed to 6-*nitro*-α-*benzamido*-3 : 4-*dimethoxycinnamic acid*, m.p. 250—251°, which is, however, further hydrolysed, not to (II), but to 6-nitrohomoveratrole. More vigorous hydrolysis (aq. KOH) yields 6-nitrohomocatechol, but if KOH–EtOH is used, Me is replaced by Et, and 6-*nitro*-3 : 4-*diethoxytoluene*, m.p. 114°, is obtained. E. W. W.

Decomposition of acetylphthalimide. C. D. Hurd, M. F. Dull, and J. W. Williams (J. Amer. Chem. Soc., 1935, **57**, 774—775).—Pyrolysis of *o*-$C_6H_4(CO)_2NAc$ gives AcOH, Ac_2O, $COMe_2$, and a little keten, but no keten dimeride (cf. A., 1932. 849). R. S. C.

Mercuration and decarboxylation of polycarboxylic acids. K. Dziewoński and W. Kahl [with W. Dymek] (Bull. Acad. Polonaise, 1934, **A**, 394—397, and Rocz. Chem., 1935, **15**, 89—91).—Mercuration and decarboxylation of *o*- and *peri*-dicarboxylic acids is effected in good yield in 1—3 hr. at 160—180°/10—20 atm. in presence of a little H_2O. At higher temp. both CO_2H may be removed. The following are obtained: BzOH from *o*-$C_6H_4(CO_2H)_2$; α-$C_{10}H_7{\cdot}CO_2H$ from 1 : 8-$C_{10}H_6(CO_2H)_2$; 3- (22·3%) and 6-OMe·$C_{10}H_6{\cdot}CO_2H$ (27·6%) from 3-methoxynaphthalic anhydride; 3- (33%) and 6-$NO_2{\cdot}C_{10}H_6{\cdot}CO_2H$ (17%) and β-$C_{10}H_7{\cdot}NO_2$ (28%) from 3-nitronaphthalic anhydride. R. S. C.

Derivatives of 1 : 4-di-α-naphthylnaphthalene. R. Weiss and J. Koltes (Monatsh., 1935, **65**, 351—356).—1 : 2-Di-α-naphthyl*iso*benzfuran (I) (improved prep.) with maleic anhydride in xylene at b.p. gives 1 : 4-*di*-α-*naphthyl*-1 : 4-*oxido*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 3-*dicarboxylic anhydride*, m.p. 243—245°, converted by cold HCl in EtOH into *Et*$_2$ 1 : 4-*dinaphthylnaphthalene*-2 : 3-*dicarboxylate*, m.p. 218—220°, hydrolysed by KOH–EtOH to 1 : 4-*di*-α-*naphthylnaphthalene*-2 : 3-*dicarboxylic anhydride* (*compound* with xylene, m.p. 282—285°). The product from (I) and acraldehyde in EtOH at b.p., when treated with dry HCl yields 1 : 4-*di*-α-*naphthyl*-2-*naphthaldehyde*, m.p. 268—270°, the *oxime*, m.p. 268—270°, of which with Ac_2O at b.p. gives the *acetyloxime*, m.p. 185—187°, which with NH_2Ph at b.p. under reduced pressure yields 1 : 4-*di*-α-*naphthyl*-2-*naphthonitrile*, m.p. 225—227°. F. R. G.

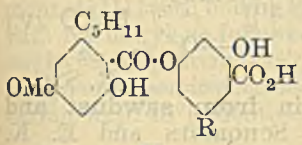
Derivatives of 0 : 3 : 3-*dicyclo*octane. J. C. Bardhan and S. K. Banerji (J.C.S., 1935, 474—476).—Condensation of Et Δ^1-*cyclo*pentenecarboxylate with CN·CHNa·CO_2Et yields α-cyano-1-carbethoxy-*cyclo*pentane-2-acetic acid (I) as well as the Et ester (II) (cf. Cook *et al.*, A., 1934, 1002). (I) on distillation under reduced pressure gives 1-*carbethoxy*cyclopentane-2-*acetonitrile*, b.p. 128°/4 mm., 265°/757 mm., and with EtOH in H_2SO_4 yields (II), the Na derivative of which with $CH_2Br{\cdot}CO_2$Et in EtOH yields *Et* α-*cyano*-α-2-*carbethoxy*-1-cyclo*pentylsuccinate*, b.p. 207°/5 mm., hydrolysed with aq. H_2SO_4 to 2-*carboxy*-1-cyclo*pentylsuccinic acid*, m.p. 202°, the *Et* ester, b.p. 172°/4 mm., of which, heated with pulverised Na in C_6H_6 for 3 hr., yields *Et* 0 : 3 : 3-dicyclo*octan*-1-*one*-2 : 3-*dicarboxylate*, b.p. 166°/6 mm., which with aq. $FeCl_3$ gives a reddish-violet colour and with aq. HCl yields the corresponding *acid*, a gum (*semicarbazone*, m.p. 210°). F. R. G.

Constitution of diploschistessic acid. G. Koller and H. Hamburg (Monatsh., 1935, **65**, 367—374).—Diploschistessic acid (I) (cf. Zopf, A., 1906, i, 672) from *Diploschistes scruposus*, L., and *D. bryophilus*, Erh., is 3-hydroxy-5-(2′ : 3′ : 4′-trihydroxy-6′-methylbenzoyl)-*o*-toluic acid, possibly mixed with 3 : 4-dihydroxy-5-(2′ : 4′-dihydroxy-6′-methylbenzoyl)-*o*-toluic acid. (I) gives an Ac_4 derivative, m.p. 157° (decomp. in evacuated tube) (*Me* ester. m.p. 162°), and with hot MeOH in a sealed tube yields orcinol and *Me* 3 : 4 : 5-*trihydroxy*-*o*-*toluate*, m.p. 155°, sublimes 140°/0·008 mm., which with conc. HI yields an oil converted at 110—130°/0·008 mm. into 5-methylpyrogallol, also formed by reduction of gallaldehyde with Zn and conc. HCl. F. R. G.

Synthesis of substances related to cochenillic and carminic acids. A. N. Meldrum and K. S. Vaidyanathan (Proc. Indian Acad. Sci., 1935, **1**, A, 510—527).—Me 5-methoxy-*m*-toluate with $CCl_3{\cdot}CHO,H_2O$ in H_2SO_4 at 50° gives 5-*methoxy*-3-*methyl*- (I), m.p. 118°, and 3-*methoxy*-5-*methyl*-2-*trichloromethylphthalide* (II), m.p. 138° (cf. J.C.S., 1911, **99**, 1712) (at 0° a product, [(I)+(II)], m.p. 116°, is obtained), hydrolysed to 5-methoxy-3-methyl- (III) and 3-methoxy-5-methyl-phthalide-2-carboxylic acid (IV). Similarly, 5-hydroxy-*m*-toluic acid affords 5-*hydroxy*-3-*methyl*- (V), m.p. 178° (*Ac* derivative, m.p. 128°), and 3-*hydroxy*-5-*methyl*-2-*trichloromethylphthalide* (VI), m.p. 184° (*Ac* derivative, m.p. 164°), which with BzCl in C_5H_5N gives (VII) (below). (V) and (VI) with hot NaOH give, respectively, 5-*hydroxy*-3-*methyl*-, m.p. 223° [methylated to (III)], and 3-*hydroxy*-5-*methyl*-*phthalide*-2-*carboxylic acid*, m.p. 214° [methylated to (IV)], which with BzCl in C_5H_5N gives 2-*benzoyl*-6-*carboxy*-4-*methylmandelic acid* (VII), m.p. 45°. (V) and (VI) with Zn–AcOH at room temp. give 5-*hydroxy*-2-, m.p. 229°, and 5-*hydroxy*-6-β-*dichloroethyl*-m-*toluic acid*, m.p. 179° (*Ac* derivative, m.p. 138°), respectively, converted by H_2SO_4 into 4-*hydroxy*-2-*carboxy*-6-*methyl*-, m.p. 210°, and 2-*hydroxy*-6-*carboxy*-4-*methyl*-*phenylacetic acid*, m.p. 254°, respectively, which with NaOH–$KMnO_4$ give β- (A., 1897, i, 539) and γ-coccinic acid (VIII), (A., 1921, i, 111). (V) with Br in AcOH at 100° gives 4 : 6-*dibromo*-5-*hydroxy*-3-*methyl*-2-*trichloromethyl phthalide*, m.p. 214°, which with warm NaOH affords 4 : 6-*dibromo*-5-*hydroxy*-3-*methylphthalide*-2-*carboxylic acid*, m.p. 268°, oxidised ($KMnO_4$–NaOH) to 4 : 6-*dibromo*-5-*hydroxy*-3-*methylphthalic acid*, m.p. 128° (*anhydride*, m.p. 197°). Similarly were obtained 4 : 6-*dibromo*-3-*hydroxy*-5-*methyl*-2-*trichloromethylphthalide*, m.p. 216°, 4 : 6-*dibromo*-3-*hydroxy*-5-*methylphthalide*-2-*carboxylic acid*, m.p. 230° (decomp.), and 4 : 6-*dibromo*-3-*hydroxy*-5-*methylphthalic acid*, m.p. 187° (decomp.) (*anhydride*, m.p. 272°). (II) with Zn–AcOH at room temp. gives 5-*methoxy*-6-β-*dichloroethyl*-m-*toluic acid*, m.p. 174°, converted by conc. H_2SO_4 into 2-*methoxy*-6-*carboxy*-4-*methylphenylacetic acid*, m.p. 209° (*anhydride*, m.p. 160°) [oxidised to the Me ether of (VIII)], which with $CCl_3{\cdot}CHO$ in H_2SO_4 gives 5-*methoxy*-3-*methyl*-2-*trichloromethyl*-6-*carboxymethylphthalide*, m.p. 241°, reduced (Zn–AcOH) to 2-*methoxy*-6-*carboxy*-4-*methyl*-5-β-*dichloroethylphenylacetic acid* (IX), m.p. 145°. (XI) with hot conc. H_2SO_4 gives 3-*methoxy*-5-*methyl*-2 : 6-*dicarboxymethylbenzoic acid* (X), m.p. 254°. (I) similarly affords the analogous series of compounds: 5-*methoxy*-2-β-*dichloroethyl*-m-*toluic acid*, m.p. 143°, 4-*methoxy*-6-*carboxy*-2-*methylphenylacetic acid*, m.p. 180° (*anhydride*, m.p. 134°); 3-*methoxy*-5-*methyl*-2-*trichloromethyl*-6-*carboxymethylphthalide*, m.p. 221°, and 4-*methoxy*-2-*methyl*-5-β-*dichloroethyl*-6-*carboxy*-

phenylacetic acid, m.p. 136°, which is converted into (X). (X) with KOH–$KMnO_4$ at 50—60° gives some cochenillic acid, m.p. 225° (A., 1897, i, 539) [identical with the acid obtained from cochineal (cf. A., 1913, i, 977)], but mainly the Me ether, m.p. 200° (cf. A., 1910, i, 487). J. L. D.

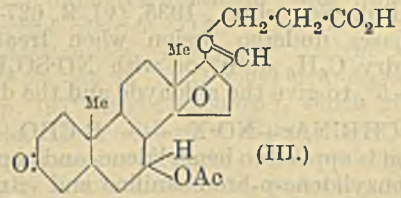
Lichen substances. L. Components of *Parmelia perlata*, Ach. Y. Asahina and F. Fuzikawa (Ber., 1935, **68**, [*B*], 634—639).—Extraction of *P. perlata*, Ach., from Europe (probably *P. cetrarioides*, Del., var. *typica*, Du Rietz) with Et_2O yields a mixture (I) of atranorin and chloroatranorin and *perlatolic acid* (*diolivetolcarboxylic acid Me*$_1$ *ether*) (II; R=C_5H_{11}), m.p. 108°, very similar except in m.p. to Zopf's imbricaric acid (III). It is hydrolysed by alkali to olivetolcarboxylic acid Me_1 ether, m.p. 126°, olivetol (IV), m.p. 41°, and CO_2. Cautious treatment with MeOH–KOH leads to Me olivetolcarboxylate *p*-Me ether (V) and olivetolcarboxylic acid. (II) is converted by CH_2N_2 and subsequent hydrolysis into olivetolcarboxylic acid Me_2 ether and olivetolcarboxylic acid *o*-Me ether. Extraction of a further sample of European *P. perlata*, Ach., scarcely differing externally from that used above, affords (I) and imbricaric acid (VI), m.p. 125—126°. (VI) is hydrolysed by KOH to (V), divarin, and CO_2 and with MeO–KOH affords (V) and divaric acid. (VI) is therefore (II) with R=Pr. Extraction of a Japanese lichen of very similar type gave (VI) and an acid, m.p. 112°, hydrolysis of which affords (IV) and (V). It is considered to be a mixture of (II) and (VI). (III) is regarded as a similar mixture from which (VI) would have been obtained if further purification had been possible, and the name "imbricaric acid" is hence assigned to (VI). H. W.


(II.)

Isomerism of *apo*cholic and dihydroxycholenic acids. K. Yamasaki (Z. physiol. Chem., 1935, **233**, 10—12).—HCl in AcOH or $CHCl_3$ converts dihydroxycholenic acid (I) into *apo*cholic acid (II), with production of some *iso*dihydroxycholenic acid (III), (cf. A., 1933, 1162). In the Hammarsten reaction of cholic acid (I) is probably first formed with elimination of H_2O, (II) being then produced and transformed into (III). W. McC.

Fate of dehydrocholic acid and dehydrodeoxycholic acid in the toad. K. Yamasaki and K. Kyogoku (Z. physiol. Chem., 1935, **233**, 29—35; cf. Shibuya, A., 1933, 974).—*iso*Reductodehydrocholic acid (*acetate*, m.p. 216—217°) on oxidation with CrO_3 yields dehydrocholic acid. The urine of toads to which Na dehydrodeoxycholate has been subcutaneously administered yields β-3-*hydroxy*-12-*ketocholanic acid*, m.p. 125°, $[\alpha]_D^{20}$ +99·89° in EtOH (*oxime* of Me ester, m.p. 100°; *acetate*, m.p. 175—179°), an isomeric *acid*, m.p. 220° (*Me* ester, m.p. 115°; *acetate*, m.p. 195—205°), and deoxybilianic acid. 12-*Hydroxy*-3-*ketocholanic acid*, m.p. 112—120° (*Me ester*, m.p. 144—145°), is obtained by hydrolysis of Me diacetyldeoxycholate (Wieland *et al.*, A., 1933, 158) to the corresponding *monoacetyl acid*, m.p. 163—167°, which is then oxidised with CrO_3 in AcOH to 12-*acetoxy*-3-*ketocholanic acid*, m.p. 95—96°. W. McC.

Constitution of the poisons of the native toad. VIII. H. Wieland and G. Hesse (Annalen, 1935, **517**, 22—34).—New analyses of bufotalin (I), m.p. 223° (decomp.) after slight softening at 150°, bufotalone (II), m.p. 287° (improved prep.), and bufotalein, m.p. 224°, confirm the presence of 24C. The aldo-enolic nature of the lactone group of (I) is established by the isolation of HCO_2H from the products of ozonisation of (I). Fission of the ring occurs very readily and the liberated CHO group is readily identified by ammoniacal Ag solution or fuchsin–H_2SO_4. The course of the change appears to be ·C<CH₂·CH₂ / CH—O>CO→·C(:CH·OH)·CH_2·CH_2·CO_2H→ ·CH(CHO)·CH_2·CH_2·CO_2H. (I) and $Ba(OH)_2$ in MeOH give the (non-homogeneous) *salt* $C_{26}H_{36}O_7Ba$, whereas under rather more drastic conditions Ac is simultaneously removed yielding the *acid*, $C_{24}H_{34}O_5$, m.p. 220° (decomp.) after softening (*Me* ester, m.p. 225—230° after softening at 185°). Treatment of (II) with $Ba(OH)_2$ in MeOH affords the (non-homogeneous) *salt*, $C_{26}H_{35}O_7Na$ (corresponding *bisdinitrophenylhydrazone*, decomp. >181°). (II) is converted by 0·05*N*-KOH in EtOH at 0°, by 0·1*N*-NaOH in


(III.)

C_5H_5N, or by Ag_2O–EtOH into *anhydrobufotalonic acid* (? III), m.p. 232—233° (decomp.), in place of the expected dicarboxylic acid. The corresponding Ac-free acid is obtained from (I). Further evidence of the existence of the same tetracyclic ring system in (I), the bile acids, and sterols is obtained by the isolation of chrysene from the products of the dehydrogenation of (I) by Se. Bufotalidin (formerly designated bufotalein), m.p. 228°, is $C_{24}H_{32}O_6$. It contains an unsaturated lactone group and gives an *Ac* derivative, $C_{26}H_{34}O_7$, m.p. 244—245° after softening and becoming yellow at 235°. It contains 3 double linkings and is free from Ac. Bufotalinin, m.p. 233°, shows only a feeble Liebermann reaction and is very unstable; Ac is present. H. W.

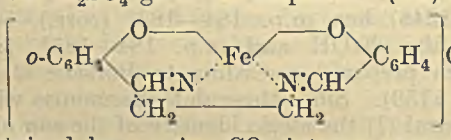
Polyterpenes and polyterpenoids. XCVII. Identity of the steric configuration of hydroxyl in position 3 in lithocholic acid and *epi*coprosterol. L. Ruzicka and M. W. Goldberg (Helv. Chem. Acta, 1935, **18**, 668—675).—Lithocholic acid (I) obtained by a modification of the method of Wieland *et al.* (A., 1932, 1248) has m.p. 184—185° (corr.), $[\alpha]_D$ +35·5° in abs. EtOH and m.p. 184—185°, $[\alpha]_D$ +33·8° when prepared according to Borsche *et al.* (A., 1922, i, 1159). Since these data harmonise with those of natural (I) the steric identity of the samples may be regarded as established. Since the synthetic acids are obtained under conditions which cause about

80% isomerisation of coprosterol to *epi*coprosterol (II), the *epi*-position of the 3-OH in (I) is highly probable, but this cannot be assumed for deoxycholic or cholic acid. Proof of the steric configuration of the 3-OH is afforded by the oxidation of acetyl-lithocholic acid to 3-*epi*hydroxyætiocholan-17-one (III), m.p. 150—151°, $[\alpha]_D$ +104·7° in abs. EtOH (semicarbazone, m.p. 253—254°), identical with that obtained from *epi*coprosteryl acetate (A., 1934, 1222). Further, reduction of Me lithocholate (IV) according to Bouveault leads to the *diol* $C_{24}H_{42}O_2$, m.p. 179—180°, $[\alpha]_D$ +35·2° in MeOH, the *diacetate* of which is oxidised to (III). (III) is converted by MgMeI in Et_2O followed by Ac_2O into *dehydronor*epi*coprosteryl acetate*, m.p. 111·5—112·5°, reduced (PtO_2 in Et_2O) to *nor*epi*coprosteryl acetate*, m.p. 93°, $[\alpha]_D$ +48·2° in C_6H_6, which is hydrolysed to nor*epi*coprosterol (V), m.p. 153—154°, $[\alpha]_D$ +29·2° in C_6H_6. 3-Hydroxy-*allo*cholan-17-one and 3-hydroxycholanone are immediately pptd. by digitonin in slightly aq. EtOH, whereas ppts. are not given by (II) or (V). The precipitability of a sterol or bile acid derivative is not incontrovertible evidence of the steric arrangement of the 3-OH. Androsterone and (I) are the only naturally occurring compounds in which the *epi*-position of OH is beyond doubt. H. W.

Action of nitrosyl chloride and nitrosylsulphuric acid on aromatic Schiff's bases. J. Turcan (Bull. Soc. chim., 1935, [v], 2, 627—632).—Schiff's bases undergo fission when treated with NOCl in dry C_6H_6 at 0° or with $NO{\cdot}SO_4H$ in dry Et_2O at −5°, to give the aldehyde and the diazonium salt: $CHR{:}NAr + NO{\cdot}X \longrightarrow R{\cdot}CHO + ArN_2{\cdot}X$. Such fission is applied to benzylidene- and heptylideneaniline, benzylidene-*p*-bromoaniline and -α-naphthylamine. Mechanisms are suggested. J. W. B.

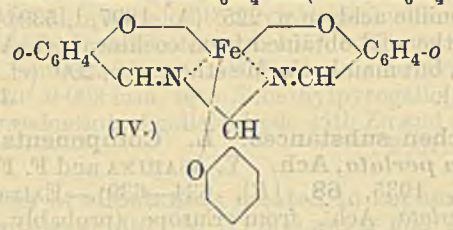
Dehydration of the hydrobenzoin of α-phenyl-β-vinylethylene glycol; formation of α-phenylcrotonaldehyde. M. Tiffeneau and P. Weill (Compt. rend., 1935, **200**, 1217—1219).—Acraldehyde with PhCHO and Zn–Cu in EtOH–H_2O gives *γδ-dihydroxy-δ-phenyl-Δ$^{\alpha}$-butylene* (I), m.p. 43°, together with some divinylethylene glycol and hydrobenzoin. (I) with boiling HCO_2H gives only *α-phenylcrotonaldehyde* (II), b.p. 117°/15 mm. (*semicarbazone*, m.p. 201°; *oxime*, m.p. 116°). The reaction mechanism is by way of α-phenyl*iso*crotonaldehyde (involving migration either of Ph or $CH_2{:}CH$), which then isomerises to (II). J. L. D.

Cyclic iron compounds formed by auxiliary valencies. T. Tsumaki (Bull. Chem. Soc. Japan, 1935, **10**, 74—81; cf. A., 1933, 824).—*o*-$OH{\cdot}C_6H_4{\cdot}CHO$ (I), $(\cdot CH_2{\cdot}NH_2)_2$, and $FeSO_4$ (II) in aq. C_5H_5N in presence of air give the *hydroxide* (III), +0·25C_5H_5N (not lost at 130°) and +2H_2O (not lost at 140°), which in dil. H_2SO_4 gives the sulphate. (III) may also be



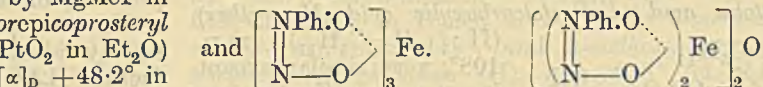
(III.)

obtained by passing CO_2 into an aq. suspension of the corresponding oxide. (I), (II), and NH_3 in aq. EtOH at 100° give the *substance* (IV), +$PhNO_2$ (lost at 150°), derived from $OH{\cdot}C_6H_4{\cdot}CH(N{:}CH{\cdot}C_6H_4{\cdot}OH)_2$



(IV.)

Cupferron and (II) in H_2O give "*phenylnitrosohydroxylamine ferric oxide*" (V), +2EtOH (lost at 110°)



(V.)

R. S. C.

Preparation of vanillin from sawdust and sulphite liquor. P. P. Schorigin and E. K. Smoljaninova (J. Gen. Chem. Russ., 1934, **4**, 1428—1433).—Kürschner's method (A., 1925, i, 1387) gives trustworthy results for determination of vanillin (I); the raw product should first be freed from volatile aldehydes by steam-distillation. Sulphite liquor gives higher yields of (I) than does sawdust, when treated by Kürschner's method. The yields are not increased when oxidising agents are present during hydrolysis, as would follow from Freudenberg's theory of the structure of lignin (A., 1933, 276). R. T.

Planar configuration for quadrivalent nickel, palladium, and platinum.—See this vol., 684.

Fused carbon rings. IV. Further investigation of 0 : 3 : 3-*dicyclo*octanones in relation to the strain theory. J. W. Barrett and R. P. Linstead (J.C.S., 1935, 436—442).—Et *cyclo*pentanone-2-acetate and $CN{\cdot}CH_2{\cdot}CO_2Et$ with piperidine give an *ester* (I), m.p. 84°, as well as Et *cyclo*pentylidenecyanoacetate-2-acetate, b.p. 172—174°/2 mm. (cf. A., 1934, 1002). (I) with conc. HCl gives, probably, the *lactone* of cyclo*pentanol*-1 : 2-*diacetic acid*, m.p. 83°, reduced by Al–Hg to Et *cyclo*pentane-1-cyanoacetate-2-acetate, and with conc. HCl gives a mixture of *cis*- and *trans-cyclo*pentane-1 : 2-diacetic acids, which with BaO at 300° gives the pure *trans*-acid (I), m.p. 133° (cf. Hückel *et al.*, this vol., 211), together with *cis*-β-0 : 3 : 3-*dicyclo*octanone (II), m.p. −33° to −34°. (I) with BaO at 340° gives *trans*-β-0 : 3 : 3-*dicyclo*octanone (III), m.p. 13—14°, the structure of which is confirmed by oxidation with conc. HNO_3 or $KMnO_4$ to *trans-cyclo*pentane-1-carboxy-2-acetic acid. The semicarbazone (IV) of (II) heated with KOH and a little MeOH gives cis-0 : 3 : 3-dicyclo*octane* (V), b.p. 136°. The (IV) of (III) heated with NaOEt gives trans-0 : 3 : 3-dicyclo*octane* (VI), b.p. 132°, m.p. −36°, and a *compound*, m.p. 188°. The lactone of *cyclo*pentanol-2-acetic acid is shown to be the *cis*-isomeride. The b.p., d_4^{18}, n_D^{18}, $[R_L]_D$, exaltation, and heats of combustion are recorded for (II), (III), (V), and (VI). F. R. G.

Synthesis of jasmone. W. Treff and H. Werner (Ber., 1935, **68**, [*B*], 640—644; cf. A., 1933, 1296).—Δ$^{\gamma}$-Hexenol (from Japanese peppermint oil and containing 7% of *n*-hexyl alcohol) is transformed

into Δ^{γ}-*hexenyl bromide*, b.p. 46—47°/13 mm., converted by NaCN in EtOH–H_2O into Δ^{γ}-heptenonitrile, b.p. 49—50°/5 mm., whence Δ^{γ}-heptenoic acid (I), b.p. 98—100°/5 mm. [oxidised by $KMnO_4$ to $(\cdot CH_2\cdot CO_2H)_2$]. The chloride, b.p. 51—53°/5 mm., of (I) is transformed by Br at room temp. and subsequently at 70—100° followed by EtOH into *Et* $\alpha\gamma\delta$-*tribromo*-n-*heptoate* (II), b.p. 155—160°/5 mm. (II) is converted by Et lævulate and activated Zn filings in C_6H_6 into the *substance* (III), $\begin{matrix}CH_2\cdot CH_2\\ CO\text{——}O\end{matrix}>CMe\cdot CH(CO_2Et)\cdot CH_2\cdot CH{:}CHEt$, b.p. 163—164°/5 mm., and a product hydrolysed to (II). Treatment of (III) with boiling EtOH–HCl and of the product with Na in xylene followed by 20% H_2SO_4 leads to 3-methyl-2-Δ^{β}-pentenyl-Δ^2-*cyclo*pentenone, b.p. 109—110°/5 mm. [semicarbazone, m.p. 204—206° (decomp.); oxime, m.p. 45°], identical with natural jasmone. H. W.

Hydroxymethylene ketones and their reaction products. VII. Synthesis of an isomeride of irone. R. E. Meyer (Helv. Chim. Acta, 1935, **18**, 470—473).—*cyclo*Geranyl Me ketone is transformed by NaOEt and HCO_2Et into the corresponding OH·CH: ketone, the Mg salt of which is converted by MgMeI into a product (I) which loses H_2O with difficulty and does not give MeCHO when distilled in vac. Treatment of the acetate of (I) with Cu powder in petroleum at 150—160° yields α-2 : 6 : 6-*trimethyl*-$\Delta^{1\ (or\ 2)}$-cyclo*hexenyl*-Δ^{γ}-*penten*-β-*one*, b.p. 134—136°/10 mm. H. W.

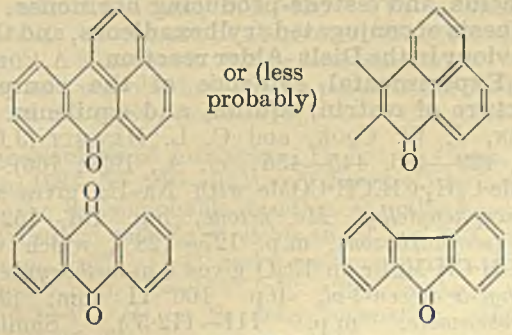
Haloform reaction. XV. Stepwise halogenation. B. A. Bull, W. E. Ross, and R. C. Fuson (J. Amer. Chem. Soc., 1935, **57**, 764—765; cf. A., 1934, 990).—Combination of steric hindrance and solubility in alkali stabilises ω-halogenoacetophenones to such an extent that every step in the successive ω-halogenation and subsequent hydrolysis of a COPhMe derivative by hypohalite can be separately realised. 2 : 4 : 6-Tribromo-3-acetylbenzonitrile (modified prep.; 35% yield) is hydrolysed [H_2SO_4–AcOH–H_2O 2 : 1 : 1 (vol.); $NaNO_2$] to 2 : 4 : 6-*tribromo*-3-*acetylbenzoic acid* (I), m.p. 192—193° (decomp.), converted by NaOBr at 0° into the (15 min.) ω-*Br*- (II), m.p. 178—179° (decomp.), (1 hr.) ωω-*Br*$_2$- (III), m.p. 187—188° (decomp.) [also obtained from (II) by NaOBr (1 hr.)], and (24 hr.) ωωω-*Br*$_3$- (IV) -compounds, m.p. 196° (decomp.) [also obtained (24 hr.) from (II) and (III)]. (I) and NaOCl at 0° (5 min.) give the ωω-*Cl*$_2$- (V), m.p. 180—181° (decomp.), and (1 hr.) ωωω-*Cl*$_3$-compound (VI), m.p. 182—183° (decomp.). (IV) and (VI) are unchanged by cold aq. NaOH (5 min.), but, when warmed, give 2 : 4 : 6-*tribromoisophthalic acid*, m.p. 275—277°, also obtained from (II), (III), and (V) by warm hypohalites. The ω-Cl-compound could not be isolated. R. S. C.

Acid degradation. M. S. Newman (J. Amer. Chem. Soc., 1935, **57**, 732—735).—Reaction of α-Br-acids with NaN_3 (modified prep.) in various solvents is described. Chlorides, CHRBr·COCl, react best in AcOH. C_5H_5N is better than C_6H_6, but removes HBr from chlorides, $CH_2R\cdot CR'Br\cdot COCl$, leading, however, eventually also to ketones. Hydrolysis of the azide is by way of the carbimide, since CHPhBr·COCl and NaN_3 yield some CHPhBr·NCO, hydrolysed by acid to PhCHO and with EtOH giving $CHPh(NH\cdot CO_2Et)_2$. α-Bromo-hexahydrobenzoyl and -*cyclo*pentylacetyl chloride (I) give ketone and aldehyde, respectively, without ring change. cyclo-*Pentanaldehyde*, from (I) or from the *glycide* ester, b.p. 90—93°/3—4 mm., from *cyclo*pentanone and $CH_2Cl\cdot CO_2Et$, has b.p. 135—136° (*dimedone* derivative, m.p. 162—163°). R. S. C.

Cleavage of unsymmetrical ketones by potassium hydroxide. I. W. E. Bachmann (J. Amer. Chem. Soc., 1935, **57**, 737—738).—By determination of the amount of each acid formed from ketones, CORR', by hot, solid KOH the following relative tenacities are calc.: *p*-, 1·38, and *m*-C_6H_4Me, 1·08; *p*-C_6H_4Ph, 1·04; Ph, 1; 3-, 0·82, and 2-phenanthryl, 0·79; *o*-C_6H_4Me, 0·22; 9-, 0·05, and 1-phenanthryl, 0·04. The orientation as well as the substituent is thus of importance. The $C_6H_4Me\cdot COPh$ and $C_6H_4Me\cdot CO\cdot C_6H_4Ph$ series give mutually consistent results. R. S. C.

Synthesis of di-*p*-xenylketen. E. Schilov and S. Burmistrov (Ber., 1935, **68**, [*B*], 582—584).—Di-*p*-diphenylyl ketone (I), m.p. 236°, from Ph_2, $COCl_2$, and $AlCl_3$, is converted by Na–Hg followed by CO_2 in Et_2O into *di*-p-*diphenylylglycollic acid* (II), m.p. 182·4—184°, which with PCl_5 in CCl_4 affords (I), dichlorodi-*p*-diphenylylmethane and *chlorodi*-p-*diphenylylacetyl chloride* (III), m.p. 109·5° [*chlorodi*-p-*diphenylylacetanilide*, m.p. 174° (slight decomp.)]. (III) and Zn–Hg in Et_2O yield *di*-p-*diphenylylketen* (IV), m.p. 197° (slight decomp.), which gives an intense green colour with conc. H_2SO_4, loses CO at 250° with formation of a strongly fluorescent material, and is unusually stable towards O_2 in boiling C_6H_6. (II) is reduced by HI and red P in AcOH to *di*-p-*diphenylylacetic acid*, m.p. 208°, whence the corresponding *chloride*, m.p. 110°, and *anilide*, m.p. 278°, also obtained from (IV) and NH_2Ph in Et_2O. H. W.

Use of Grignard reagent for locating certain ethylenic linkings in polynuclear ring systems. I. Benzanthrone. C. F. H. Allen and S. C. Overbaugh (J. Amer. Chem. Soc., 1935, **57**, 740—744).—Cases of 1 : 6-addition of Grignard reagents to benzanthrone (I) are disproved. 1 : 4-Addition is normal for (I), but 1 : 2-addition occurs with anthrone, anthraquinone, and fluorenone. The structures given below are thus indicated, at least in Et_2O. "Diene" syntheses are of diagnostic val. only when positive.



(I) (modified prep.) gives (Grignard; 3 mols. of reagent in Et_2O) 4-*phenyl*- (II) (42%), m.p. 186°, 4-

benzyl- (III) (22%), m.p. 135°, and 4-*heptyl-benzanthrone* (61% yield), m.p. 77—78°. Structures are proved as follows. (II) and $KMnO_4$ give 4-*phenylanthraquinone*-1-*carboxylic acid*, m.p. 288—290° (decomp.) [*Me* ester, m.p. 197—198° (IV)], decarboxylated by Cu at 140—160° to 1-phenylanthraquinone. Me cinnamylideneacetate and α-naphthaquinone give (IV) and *Me* 4-*phenyl*-1 : 2 : 3 : 4-*tetrahydroanthraquinone*-1-*carboxylate*, m.p. 164—165°. (II) and CrO_3–AcOH give an acid, $C_{21}H_{12}O_4$, m.p. 286—288° (decomp.), probably not an anthraquinone derivative [*Me* ester, m.p. 216—217° (cf. lit.)]. (III) and CrO_3 give 4-*benzoylanthraquinone*-1-*carboxylic acid* (75% yield), m.p. 275—278° (decomp.) (*Me* ester, m.p. 184—185°), leading to 1-benzoyl- and 1 : 4-dibenzoyl-anthraquinone, m.p. 225—227°. The prep. of (II), (III), etc. leads to much tar, which may contain some 1 : 2-additive product and certainly contains some reduced compounds, since treatment with benzoquinone gives a vigorous reaction leading to more substituted benzanthrone. MgBuγCl and (I) give by 1 : 2-addition 10-tert.-*butylbenzanthren*-10-*ol* (20%), m.p. 140° (*Et ether*, m.p. 159—160°), oxidised by CrO_3 to anthraquinone-1-carboxylic acid, m.p. 286—288° (decomp.) (Me ester, m.p. 188—190°). R. S. C.

Dioximes. CVI. E. Durio (Gazzetta, 1935, 65, 89—94).—The dioximes of glyoxal and its Me, Me_2, and Me CH_2Ph homologues, with $NHPh{\cdot}NH_2$ at 150—170°, yield the corresponding osazones. At the same temp., aminoethyl- and α- and β-aminophenyl-glyoximes fail to react. The α-form of γ-benzildioxime yields β-benzilosazone, but the β-form does not react. The α-form of phenylglyoxime yields *phenylglyoxal*-α-*osazone*, m.p. 156—157° (decomp.), and, with $C_6H_3Br{\cdot}NH{\cdot}NH_2$, *phenylglyoxal*-α-p-*bromoosazone*, m.p. 203° (decomp.); the β-form yields the osazone of m.p. 154°, now named *phenylglyoxal*-β-*osazone* (*Ac* derivative, m.p. 204—205°). The β-form of *p*-tolylglyoxime gives p-*tolylglyoxal*-β-*osazone*, m.p. 167—168° (decomp.); the α-form, a mixture of the latter with p-*tolylglyoxal*-α-*osazone*, m.p. 145°. E. W. W.

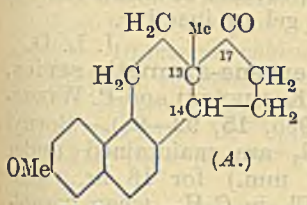
Compounds of palladium with benzylmethylglyoxime. F. P. Dwyer and D. P. Mellor (J. Amer. Chem. Soc., 1935, 57, 605—607).—The prep. and properties of *cis*- and *trans*-isomerides of *Pd bis*-anti-*benzylmethylglyoxime* (m.p. 207—208° and 175°, respectively) are described. E. S. H.

Synthesis of compounds related to the sterols, bile acids, and œstrus-producing hormones. V. Synthesis of conjugated arylhexadienes, and their behaviour in the Diels–Alder reaction. A. Cohen. **VI. Experimental evidence of the complete structure of œstrin, equilin, and equilenin.** A. Cohen, J. W. Cook, and C. L. Hewett (J.C.S., 1935, 429—436, 445—455; cf. A., 1934, 766).—V. *m*-$OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COMe$ with Na–Hg gives β-m-*methoxyphenylethyl Me ketone*, b.p. 151—152°/10 mm. (*semicarbazone*, m.p. 127—128°), which with $CH_2{:}CH{\cdot}CH{\cdot}MgBr$ in Et_2O gives ζ-m-*methoxyphenyl*-δ-*methyl*-Δ$^{\alpha}$-*hexen*-δ-*ol*, b.p. 166°/11 mm. (3 : 5-*dinitrobenzoate*, m.p. 111—112·5°). Similarly $CH_2Ph{\cdot}CH_2{\cdot}CHO$ and $CH_2Ph{\cdot}CH_2{\cdot}COMe$ yield, respectively, ζ-*phenyl*-Δ$^{\alpha}$-*hexen*-δ-*ol*, b.p. 130°/11 mm. (3 : 5-*dinitrobenzoate*, m.p. 82—83°), and ζ-*phenyl*-δ-*methyl*-Δ$^{\alpha}$-*hexen*-δ-*ol*, b.p. 135°/13 mm. (3 : 5-*dinitrobenzoate*, m.p. 80—81°), converted by $KHSO_4$ at 140—145° (45 min.) into ζ-*phenyl*-δ-*methyl*-Δ$^{\alpha\gamma}$-*hexadiene*, b.p. 116°/12 mm. *Me*, b.p. 148°/15 mm., and *Et* β-m-*methoxyphenylpropionate*, b.p. 156—157°/15 mm., with Na in EtOH give γ-m-*methoxyphenyl*-n-*propyl alcohol* (I), b.p. 155—157°/15 mm. (3 : 5-*dinitrobenzoate*, m.p. 69—70°), also obtained in poor yield from *m*-$OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2Me$ with Na and EtOH. $CH_2{:}CH{\cdot}CHO$ and the Mg derivatives of the *chloride*, b.p. 137°/15 mm., from (I) and of γ-phenyl-*n*-propyl chloride in Et_2O give, respectively, ζ-m-*methoxyphenyl*-Δ$^{\alpha}$-*hexen*-γ-*ol*, b.p. 177°/14 mm. (3 : 5-*dinitrobenzoate*, m.p. 106—107°), and ζ-*phenyl*-Δ$^{\alpha}$-*hexen*-γ-*ol*, b.p. 135°/12 mm. (3 : 5-*dinitrobenzoate*, m.p. 113—114°), which with $KHSO_4$ give, respectively, ζ-m-*methoxyphenyl*-, b.p. 149/18 mm., and ζ-*phenyl*-Δ$^{\alpha\gamma}$-*hexadiene*, b.p. 99·5—100·5°/11 mm. This last, but not the other dienes, reacts with maleic anhydride in warm xylene to give 3-β-*phenylethyl*-1 : 2 : 3 : 6-*tetrahydrophthalic anhydride*, m.p. 123—125° [*K H* salt+$2H_2O$, cryst.; *Me H* ester (II), m.p. 137—138°; Me_2 ester, b.p. 155—160°/0·1 mm.], which with AcOH and H_2SO_4 at 100° gives an oil and this with Se yields 3-β-*phenylethylphthalic anhydride*, m.p. 153—154° (softens 148°), sublimes 170°/0·1 mm. [also obtained by dehydrogenation with Pt-black of the product from (II) and 85% H_2SO_4].

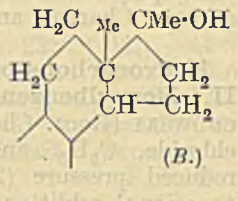
VI. β-6-*Methoxy*-1-*naphthylethyl bromide* (III), b.p. 155°/0·4 mm., m.p. 57—58° [from the alcohol (improved prep.) and PBr_3], heated (3—4 hr.) with Et 5-methyl*cyclo*pentanone-6-carboxylate (cf. Cornubert *et al.*, A., 1930, 776) and finely-divided K in C_6H_6 gives *Et* 2-(β-6′-*methoxy*-1′-*naphthylethyl*)-5-*methyl*-cyclo*pentanone*-2-*carboxylate*, b.p. 212°/0·2 mm. (*semicarbazone*, m.p. 161—163°), which with 50% aq. H_2SO_4 yields 7-*methoxy*-1′-*methyl*-1 : 2-cyclo*pentenophenanthrene*, m.p. 97·5—98° [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 129°]. Similarly Et 4-methyl*cyclo*pentanone-2-carboxylate (cf. Dieckmann, A., 1901, i, 539) gives *Et* 2-(β-6′-*methoxy*-1′-*naphthylethyl*)-4-*methyl*cyclo*pentanone*-2-*carboxylate*, b.p. about 205°/0·05—0·1 mm., and 7-*methoxy*-2′-*methyl*-1 : 2-cyclo*pentenophenanthrene*, m.p. 136·5—137·5° [*s*-$C_6H_3(NO_3)_2$ *compound*, m.p. 132—133°]. The Mg derivative of (III) with 2 : 5-dimethyl*cyclo*pentanone in dry Et_2O gives a carbinol, b.p. 160—200°/0·5 mm., converted by $KHSO_4$ at 160° (1 hr.) into 1-(β-6′-*methoxy*-1′-*naphthylethyl*)-2 : 5-*dimethyl*-Δ^1-cyclo*pentene*, b.p. 164—169°/0·4 mm. (*picrate*, m.p. 80—82°), which with $AlCl_3$ in CS_2 at 0° (5 hr.) yields 7-*methoxy*-1 : 3′-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentenophenanthrene*, b.p. 175°/0·2 mm. [*picrate*, m.p. 87—88°; *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 98°], which is converted by Se at 300—310° (15 hr.) into 7-*methoxy*-3′-*methyl*-1 : 2-cyclo*pentenophenanthrene* (IV), m.p. 146·5—148·5°, sublimes 150—160°/0·1 mm. [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 135·5—136·5°]. 2 : 2-Dimethyl*cyclo*pentanone and $Et_2C_2O_4$ with NaOEt in EtOH yields *Et* 2 : 2-*dimethyl*cyclo*pentanone*-5-*glyoxylate* (V), b.p. 141°/12 mm. (brownish-red colour with $FeCl_3$), hydrolysed to 2 : 2-*dimethyl*cyclo*pentanone*-5-*glyoxylic acid*, m.p. 75—76°. (V) boiled with K in C_6H_6 and MeI (5 hr.) gives *Et* 2 : 2 : 5-*trimethyl*cyclo*pentanone*-5-*glyoxylate*,

b.p. 135°/10 mm., hydrolysed by conc. HCl to 2 : 2 : 5-trimethyl*cyclo*pentanone, which with the Mg derivative of (III) in dry Et_2O gives 5-*ethylnerolin*, b.p. 120—130°/0·5 mm., 165°/10 mm., m.p. 54—55° (*picrate*, m.p. 83—84°), and a carbinol, b.p. > 190°/0·3 mm., converted by successive treatment with $KHSO_4$ at 160°, $AlCl_3$ in CS_2, and Se at 300—320° (13 hr.) into 7-*methoxy*-3 : 3′-*dimethyl*-1 : 2-cyclo*pentenophenanthrene* (VI), m.p. 165—165·5° [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 170—171·5°]. 7-Methoxy-1-methyl-1 : 2 : 3 : 4-tetrahydro-1 : 2-*cyclo*pentenophenanthrene with NaOEt in EtOH at 190—195° (20 hr.) yields 7-*hydroxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentenophenanthrene*, m.p. 131·5—132° (*benzoate*, m.p. 141—141·5°, sublimes 170°).

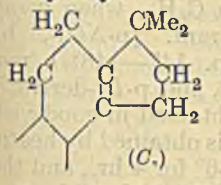
The Me ether (*A*) of equilenin (VII) with MeMgI in Et_2O gives the *methylcarbinol* (*B*), m.p. 133—133·5°, dehydrated with $KHSO_4$ at 160—170° (1 hr.) to a *compound* $C_{20}H_{22}O$ (*C*), m.p. 131—132°, hydrogenated (Pd-black, moist Et_2O) to a *compound* $C_{20}H_{24}O$ (*D*), m.p. 131—132°, converted by Se at 300—310° for 17 hr. into (VI).



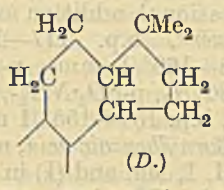
(*A*.)



(*B*.)



(*C*.)



(*D*.)

Similarly the *Me ether*, m.p. 160·5—161·5°, of equilin (VIII) gives a *methylcarbinol*, m.p. 133—134°, dehydrated to a *compound* $C_{20}H_{21}O$, m.p. 112—117°, converted by Se at 295—305° (7 hr.) into (VI); the Me ether (cf. Butenandt *et al.*, A., 1932, 781) of œstrone (IX) also yields a *methylcarbinol*, m.p. 95—100°, dehydrated to a *compound* $C_{20}H_{26}O$, m.p. 58—60°, possibly a mixture of isomerides, hydrogenated to a gum which with Se at 300—320° (21·5 hr.) yields (VI), showing that (VII), (VIII), and (IX) have a keto-group at C_{17} and a quaternary Me at C_{13} which migrates to C_{17} during dehydration with $KHSO_4$. The *Me ether* of trihydroxyœstratriene with $ZnCl_2$ at 170—180° (0·5 hr.) gave a product which with Se at 295—305° (8·5 hr.) yields (IV), the quaternary Me group migrating as above, proving its attachment at C_{13} and not C_{14}. F. R. G.

Isomerisation of hydroxyketones. "Phenylketol," COPh·CH(OH)·CH_2·COMe. M. Henze (Z. physiol. Chem., 1935, **232**, 117—122).—NaOEt in EtOH converts "phenylketol" into the *isomeride* (I), OH·CHPh·CO·CH_2·COMe, m.p. 59—59·5°, and a *compound*, $C_{22}H_{20}O_4$, m.p. 248° (*Cu* salt, m.p. 147°). With $NHPh·NH_2$, (I) gives the *pyrazole*, m.p. 115° (*acetate*, m.p. 93°). With aq. NaOH (I) affords BzOH, OH·CHPh·CO_2H, and CHPhAc·OH. The possible mechanism of the isomeric change is discussed. J. H. B.

Cyclic compounds from aromatic diamines and chloral. R. Weiss and L. Chledowski (Monatsh., 1935, **65**, 357—366).—*oo*′-Diaminodiphenyl and CCl_3·CHO heated in C_6H_6 give a *trichloroethylidene* derivative, m.p. 111°, shown to be $CCl_3·CH<^{NH·C_6H_4}_{NH·C_6H_4}$ (I), by the formation of a $(NO)_2$-derivative, m.p. 133° (decomp.). *m*-$C_6H_4(COCl)_2$ and PhOMe with $AlCl_3$ in CS_2 yield a mixture of 4 : 4′-*dimethoxy*-m- (II), m.p. 146—149°, and 4 : 4′-*dimethoxy*-p-, m.p. 239°, *-dibenzoylbenzene*, the latter being also given by *p*-$C_6H_4(COCl)_2$. (II) with HBr in AcOH at b.p. gives 4 : 4′-*dihydroxy*-m-*dibenzoylbenzene* (III) (*dihydrate*, m.p. 215°) and with HNO_3 in AcOH gives as by-product 3′-*nitro*-4′-*hydroxy*-m-*benzoylbenzoic acid*, m.p. 231° (*Et* ester, m.p. 130°), and as main product, 3 : 3′-*dinitro*-4 : 4′-*dimethoxy*-m-*dibenzoylbenzene* (IV), m.p. 174—177°, which with HBr in AcOH yields 3 : 3′-*dinitro*-4 : 4′-*dihydroxy*-m-*dibenzoylbenzene*, m.p. 195°, also given by (III) and aq. HNO_3. (IV) is reduced by aq. $(NH_4)_2S$ to 3 : 3′-*diamino*-4 : 4′-*dimethoxy*-m-*dibenzoylbenzene*, m.p. 189° (Ac_2 derivative, m.p. 201°; Ac_4 derivative, m.p. 185°), which heated with CCl_3·CHO in $CHCl_3$ gives s-*trichloroethylidene*-3 : 3′-*diamino*-4 : 4′-*dimethoxy*-m-*dibenzoylbenzene*, m.p. 200° (decomp.), which is considered to be a cyclic compound of the same type as (I). F. R. G.

Constitution and structure of chitin. K. H. Meyer and G. W. Pankow (Helv. Chim. Acta, 1935, **18**, 589—598).—Detailed röntgenographic measurements of chitin are recorded and an arrangement of the chitobiose residues in the elementary cell of chitin is suggested. H. W.

Decomposition products of substances containing uronic acid, by heating in autoclave. I. K. Aso (J. Agric. Chem. Soc. Japan, 1934, **10**, 1189—1200).—Alginic acid heated for 3 hr. (autoclave) at 160° yields alginetin (I), $C_{10}H_8O_4$, m.p. 235° [*diacetate*, m.p. 125°; *dibenzoate*, m.p. 187°; *Me*$_4$ derivative (II), m.p. 215°; *monoacetylmonomethyl* derivative, m.p. 171°]. Oxidation of (I) with H_2O_2 affords 2 : 3-dihydroxybenzoic acid (III), whilst alkali fusion yields pyrocatechol, AcOH, and (III). (II) with H_2O_2 yields 2-hydroxy-3-methoxybenzoic acid (IV). The *Me*$_2$ derivative (V) of (I) yields (IV) with H_2O_2 and with EtOH–KOH a phenolic *substance* (VI), m.p. 66°, AcOH, and (IV). (VI) (possibly 2-hydroxy-3 : ω-dimethoxyacetophenone) has two OMe groups and yields an oxime, m.p. 126°. (V) is obtained from (VI) by means of Ac_2O and NaOAc. (I) is possibly 2-methyl-3 : 8-dihydroxychromone. Reductic acid was obtained from a polyuronate by heating with dil. H_2SO_4 (autoclave). Ch. Abs. (*r*)

Constitution of miliacin. H. Ito (J. Chem. Soc. Japan, 1934, **55**, 910—913).—*Miliacin* (I) is isolated from the unsaponifiable fraction of millet-seed oil; when distilled with Zn, it yields an *oil*, b.p. 283—289°/0·76 mm., $[\alpha]_D^{26}$ +11·4°, and a resinous mixture of two *substances*, m.p. 116—118°, $[\alpha]_D^{17}$ +26·8°, and m.p. 187°, $[\alpha]_D^{11}$ +18·4°. (I) on Se dehydrogenation affords a *liquid*, $C_{13}H_{14}$(?) (*picrate*, m.p. 131°), and a *substance*, m.p. 187—188°, $[\alpha]_D^{15}$ −21·4°. Ch. Abs. (*r*)

Composition of *Salvia miltiorrhiza*. I. (Chinese drug, tan-shin.) M. NAKAO and T. FUKUSHIMA (J. Pharm. Soc. Japan, 1934, **54**, 844—858).—The three cryst. substances isolated from the EtOH extract of tan-shin are termed *tanshinones* and it is suggested that they are derived from an *o*-diketone; colour reactions are described. *Tanshinone* I (I), $C_{18}H_{12}O_3$, m.p. 231° (*quinoxaline*, m.p. 218—219°; *oxime*, m.p. 169—171°; *acetate*, m.p. 204—207°; *quinol*, m.p. 75—85°), affords an *acid*, $C_{18}H_{14}O_5$ (dibasic?), m.p. 265° (*anhydride*, m.p. 185°), which on oxidation yields a dibasic *acid* (II), $C_{13}H_{10}O_4$, m.p. 193°, and an *acid*, $C_{18}H_{12}O_{5 \text{ or } 6}$, m.p. 319°; yielding (II) and a neutral *substance*, m.p. 110—120°, with EtOH–KOH. *Tanshinone* II, $C_{19}H_{18}O_3$, m.p. 216° (*quinoxaline*, m.p. 206°; *oxime*, m.p. 198°), is more sol. than (I). *Tanshinone* III, $C_{19}H_{20}O_3$, m.p. 182° (*quinoxaline*, m.p. 149°; *oxime*, m.p. 170—172°), is even more sol.

CH. ABS. (*r*)

Cardiac glucosides. XI. Identity of α-scillanic acid with *allo*cholanic acid. A. STOLL, A. HOFMANN, and A. HELFENSTEIN (Helv. Chim. Acta, 1935, **18**, 644—659; see this vol., 609).—Scillaridin *A* is best converted by sublimation in vac. into anhydroscillaridin *A*, which is hydrogenated (PtO_2 in AcOH) to scillanic acid (I) and decahydroanhydroscillaridin. Repeated crystallisation of (I) from AcOH raises the m.p. to 165—166°. Treatment of this acid with CH_2N_2 and purification of the product from MeOH affords *Me* α-*scillanate* (II), m.p. 94° (which does not depress the m.p. of Me *allo*cholanate), and *Me* β-*scillanate* (III), m.p. 72—74°. *Pr*$^{\alpha}$ *scillanate*, m.p. 104°, does not depress the m.p. of Pr$^{\alpha}$ *allo*cholanate. Hydrolysis of (II) yields α-*scillanic acid*, m.p. 172—173°, identical with *allo*cholanic acid. β-*Scillanic acid*, m.p. 143—145°, is derived from (III). The prep. of pure *allo*cholanic acid and its derivatives and of cholanic acid is described. Sufficient evidence is not available to enable a decision to be made between the C_{24} and C_{25} formulation of (I). H. W.

Saponins. O. DAFERT [with F. BAUER, M. BAUER, V. CAPESIUS, and S. GREIFINGER]. **Saponin and sapogenin of *Chenopodium ambrosioides*, L.** O. DAFERT [with V. CAPESIUS and S. GREIFINGER] (Sci. Pharm., 1934, **5**, 84—86; Chem. Zentr., 1934, ii, 3389; cf. this vol., 348).—All parts of *C. ambrosioides* contain a saponin (I), the distribution of which is discussed. (I) is isolated by extraction with EtOH and purified by extraction with Et_2O; it contains a free CO_2H. Hydrolysis of (I) (HCl) affords *chenopodiumsapogenin* (II), $C_{30}H_{48}O_4$, m.p. 271—272° (*K* salt; Ac_1 derivative, m.p. 180°; Br_2-compound, $C_{30}H_{46}O_4Br_2$, m.p. 210°). (II) gives the Liebermann reaction and contains one CO_2H and two OH; treatment with EtOH–HCl gives a *substance*, $C_{28}H_{44}O_4$, m.p. 376°, and another *substance*, m.p. 208°.

H. N. R.

[Sulphite liquor lactone and tsugaresinol.] K. H. SLOTTA (Helv. Chem. Acta, 1935, **18**, 701).—Comment on the publication of Emde *et al.* (this vol., 623). H. W.

Constitution of lac. Pure lac resin.—See B., 1935, 465.

Transformation of rhodoxanthin into zeaxanthin. P. KARRER and U. SOLMSSEN (Helv. Chim. Acta, 1935, **18**, 477—480).—Reduction of dihydrorhodoxanthin in C_6H_6 with $Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$ gives zeaxanthin, m.p. 205° (*acetate*, m.p. 154—155°).

H. W.

Amber. III. L. SCHMID and H. KÖRPETH (Monatsh., 1935, **65**, 348—350; cf. A., 1933, 831).—The trimethylnaphthalene from the EtOH-insol. portion of amber with Se, is 1 : 2 : 5-$C_{10}H_5Me_3$ (cf. Ruzicka and Hosking, A., 1931, 231) oxidised with aq. $KMnO_4$ to 1 : 2 : 3-$C_6H_3(CO_2H)_3$ and 1 : 2 : 3 : 4-$C_6H_2(CO_2H)_4$. F. R. G.

Autoxidation of α-pinene and catalysts related thereto. K. SUZUKI (Bull. Inst. Phys. Chem. Res. Japan, 1935, **14**, 179—191).—The oxidation of *d*-α-pinene is strongly catalysed by the oxides and many salts of Pb, Co, and Mn, to give, above 40°, verbenone (I) and a polymeride; below 20°, a gum containing mainly an unsaturated peroxide which decomposes at 140° to a mixture of verbenol, (I), and a polymeride. Pt, Ag, Cr, and Tl oxides are less active. Charcoal and SiO_2 gel are inactive.

J. L. D.

Hydrocarbons of the terpene-aromatic series. II. Bornylbenzene. L. KAMIEŃSKI and P. WIERZCHOWSKI (Rocz. Chem., 1935, **15**, 92—98).—Bornyl chloride, C_6H_6, and $AlCl_3$ are maintained under reduced pressure (20—30 mm.) for 18 hr., with occasional addition of $AlCl_3$ in C_6H_6, when *bornylbenzene*, b.p. 117—118°/1·5 mm. [p-NO_2-, b.p. 168—169°/1 mm., p-NH_2-, b.p. 147—148°/1 mm., p-SO_3H-, p-SO_2·NH_2-, m.p. 167°, and p-*Br*-derivative (I), b.p. 154—155°/1 mm.], is obtained in good yield. p-*Bornylbenzoic acid*, m.p. 195°, is obtained by heating MeI, I, Mg, and (I) in Et_2O at 36° for 4 hr., and then passing CO_2 through the mixture at 0° for 3 hr.

R. T.

Pasteur's principle of molecular dissymmetry. Dextro- and lævo-camphoric acids.—See this vol., 684.

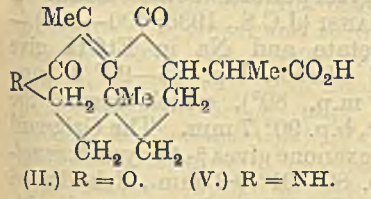
Reactions of the α-mononitrile of camphoric acid. F. SALMON-LEGAGNEUR (Compt. rend., 1935, **200**, 1222—1224).—The chloride of camphoro-α-nitrile (I) with $AlCl_3$ in $CHCl_3$ affords 3-*cyano*-1 : 1 : 2-*trimethyl*-Δ^2-cyclo*pentene*, b.p. 86—88°/11 mm. (hydrolysed to *iso*lauronolamide), which is different from the product obtained in C_6H_6 solution (cf. A., 1927, 1081). (I) with $CHNa(CO_2Et)_2$ and ZnPhBr in C_6H_6 gives, respectively, *Et* 3-*cyano*-1 : 2 : 2-*trimethyl*-cyclo*pentanoylmalonate* (II), m.p. 53°, and -cyclo*pentyl Ph ketone* (III), m.p. 93—94°. (III) is easily hydrolysed to the *amide*, m.p. 150—170° (decomp.), further hydrolysed to the acid (IV) with difficulty. (II), (III), or (IV) does not give an oxime or semicarbazone. (I) with excess of MgPhBr (cf. A., 1926, 613) gives 3-*cyano*-, m.p. 161—162° [also obtained from MgPhBr and (III)], 3-*benzoyl*-1-*hydroxybenzhydryl*-1 : 2 : 2-*trimethyl*cyclo*pentane*, m.p. 141—142°, and a small amount of 1 : 3-*dibenzoyl*-1 : 2 : 2-*trimethyl*-cyclo*pentane*, m.p. 118°. J. L. D.

New oxidation product of camphor. K. MIYAKE (Proc. Imp. Acad. Tokyo, 1935, **11**, 106—109).—Camphor and CrO_3–AcOH–Ac_2O at 60—80° give

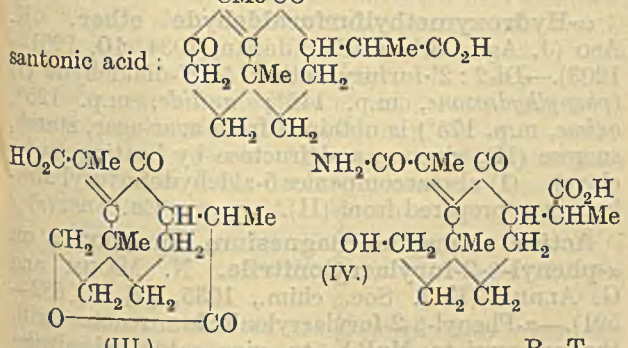
camphorquinone (traces), 5- (6%) and impure 6-*ketocamphor* (I) (18%), m.p. about 180° (*dioxime*, m.p. 241—242°, α 0°). (I) with 2% HCl or 5% Na_2CO_3 at 60° gives dl-4-*keto*-2 : 2 : 3-*trimethylcyclopentane*-1-*acetic acid*, m.p. 65—66° [*semicarbazone*, m.p. 240°; *oxime*, m.p. 185°; *Me* ester, b.p. 126°/1 mm., 223°/760 mm. (*semicarbazone*, m.p. 186°)], resolved by quinine to the l-*form*, an oil, $[\alpha]_D^{15}$ −77·5° (*semicarbazone*, m.p. 240°; *oxime*, m.p. 184°); the *d*-form, from campholenonitrile, has $[\alpha]_D^{15}$ +79·17° and gives derivatives with identical m.p. R. S. C.

Mercury derivatives of camphor. II. J. D. Loudon (J.C.S., 1935, 535—536).—3-*Chloro*- (I), m.p. 157° (decomp.), and 3-*bromo-camphor*-10-, m.p. 165° (decomp.), and 3-*chloro*- and 3-*bromo-camphor*-π-*sulphinic acid*, m.p. 149° (decomp.), are prepared from the corresponding acid chlorides and Na_2SO_3. (I) and $HgCl_2$ in C_5H_5N give 3-*chlorocamphor*-10-*mercuri-chloride*, m.p. 218—219°, $[\alpha]_{5461}^{16}$ +5·0° in $CHCl_3$, which with Cu forms *bis*-3-*chlorocamphor*-10-*mercury*, m.p. 175°, $[\alpha]_{5461}^{16}$ −22·8° in C_5H_5N, with Br–KBr affords 3-chloro-10-bromocamphor, and with I yields 3-*chloro*-10-*iodocamphor*, m.p. 89°. 3-*Bromo-camphor*-10-*mercuri-chloride*, m.p. 232°, $[\alpha]_{5461}^{16}$ +44·8° in C_5H_5N, -*bromide*, m.p. 195°, and -*iodide*, m.p. 173°, *bis*-3-*bromocamphor*-10-*mercury*, m.p. 188—189°, $[\alpha]_{5461}^{16}$ +29·13° in C_5H_5N, and 3-*bromo*-10-*iodo-camphor*, m.p. 88—89°, are similarly prepared. F. R. S.

Structure of santonin and santonic acid. A. Abkin and S. Medvedev (J. Gen. Chem. Russ., 1934, 4, 1407—1414).—Santonin (I) and liquid NH_3 (3 days; room temp.) yield the *amide*, m.p. 162—163° (decomp.), $[\alpha]_D^{23}$ −15·33° in EtOH, of santoninic acid. Santonic acid, prepared in 60% yield from (I) and aq. $Ba(OH)_2$, when oxidised with $(NH_4)_2S_2O_8$ yields a *lactone* (II), m.p. 233—234°, $[\alpha]_D^{24}$ −23·46° in EtOH, converted into the isomeric *lactone* (III), m.p. 142·5—143°, $[\alpha]_D^{22\cdot5}$ +159·87° in EtOH, by heating with aq. NaOH. (II) and liquid NH_3 (30 min.; room temp.) yield the *amide* (IV), m.p. 194—195° (decomp.), $[\alpha]_D^{23}$ +62·55° in EtOH, which affords the *lactam* (V), m.p. 217—217·5°, $[\alpha]_D^{23}$ +133·2° in EtOH, when heated at 75—80° with 5% aq. NaOH. The above results indicate the following structure for santonic acid:



(II.) R = O. (V.) R = NH.



(III.)

(IV.)

R. T.

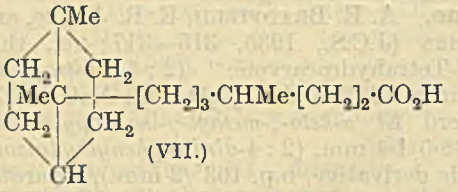
3 E

Methylsantene compounds derived from fenchyl alcohol. N. J. Toivonen (Suomen Kem., 1935, 8, B, 10—12).—Isolation of mesantenol (I), b.p. 105°/25 mm., from mesantene (A., 1930, 348) is best effected by treatment with AcOH–H_2SO_4 until 30—35% esterification has occurred; the alcohol obtained by hydrolysis of the acetate is purified through its *H phthalate*, m.p. 105—106°. Oxidation of (I) with $Na_2Cr_2O_7$–aq. H_2SO_4 affords *mesantenone*, b.p. 201°, α_D −0·12° (10 cm.), purified through its *semicarbazone*, m.p. 206—207°. J. W. B.

Syntheses in the sesquiterpene series. II. Condensation of ethyl oxalate and tetrahydrocarvone. A. E. Bradfield, E. R. Jones, and J. L. Simonsen (J.C.S., 1935, 315—317; cf. this vol., 88).—*l*-Tetrahydrocarvone (2 : 4-*dinitrophenylhydrazone*, m.p. 133°) and $Et_2C_2O_4$ and NaOEt–EtOH at 0° afford *Et* α-*keto*-ζ-*methyl*-γ-*isopropylsuberate* (I), b.p. 148·5/1·4 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 50°; *Ac* derivative, b.p. 163°/2 mm.), separated from unchanged materials by hydrolysis (MeOH–KOH) to the acid (II) (*Ag* salt; *Me* ester, b.p. 153°/2·5 mm.) and subsequent esterification (EtOH–H_2SO_4). A cyclic β-ketonic ester (cf. A., 1913, i, 1066) is not formed owing to the fission even at 0° of the intermediate glyoxylic ester by NaOEt to (I). (I) is a mixture of the ketonic and enolic forms; its $[R_L]$ suggests that it is mainly enolic. Oxidation of (II) with H_2O_2–NaOH affords *d*-α-methyl-δ-*iso*propylpimelic acid (cf. A., 1921, i, 37) (*diamide*, m.p. 181—182°; *di*-p-*toluidide*, m.p. 156—157°). (II) with H_2SO_4 at 80—85° gives the *lactone* of Δ^1-*menthen*-2-*ol*-3-*glyoxylic acid*, m.p. 115° (2 : 4-*dinitrophenylhydrazone*, decomp. 95°). Under similar conditions *l*-menthone and $Et_2C_2O_4$ gave Et menthone-2-carboxylate and a little Δ^3-menthen-3-ol-2-glyoxylolactone, m.p. 138° (lit. 142·5°) (cf. A., 1913, i, 1066). No ring fission occurred. H. G. M.

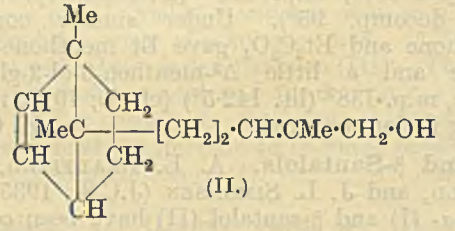
α- and β-Santalols. A. E. Bradfield, A. R. Penfold, and J. L. Simonsen (J.C.S., 1935, 309—315).—α- (I) and β-santalol (II) have been obtained pure by distilling Mysore *Santalum album* oil. (I) has b.p. 166—167°/14 mm., α_{5461} +10·3° (lit. α_D +1°) [allophanate, m.p. 162—163°; strychnine salt of the H phthalate, m.p. 144—145° (lit. 155°)]. (I) oxidised by O_3 gives $CH_2Ac{\cdot}OH$, tricyclo*ekasantalic acid* (III), and tricyclo*ekasantalal* [semicarbazone, m.p. 163—164° (lit. about 156°)]. (I) with $SOCl_2$ and C_5H_5N gives α-*santalyl chloride* (IV), b.p. 155—158°/14 mm., oxidised ($KMnO_4$) to (III) and a chloroketone, b.p. 150—160°/17 mm., and with O_3 gives CH_2O. (IV) and $CHNa(CO_2Et)_2$ give *Et* α-*santalylmalonate*, b.p. 212—213°/13 mm., hydrolysed to the *acid* (V), m.p. 120—121° (*K* salt), which loses CO_2 at 160—180° to give α-*santalylacetic acid* (VI), b.p. 188°/2 mm. (V) is oxidised by $KMnO_4$ to β-*keto*-δ-*teresantalylbutylmalonic acid* (*semicarbazone*, decomp. 172—173°), and by O_3 to (III), no keto-acid being detected. (VI) is oxidised by $KMnO_4$ to γ-*keto*-ε-*teresantalylhexoic acid*, $C_{16}H_{24}O_3$ (*Me* ester, b.p. 211°/17 mm.; *semicarbazone*, m.p. 176—177°, and *phenylsemicarbazone*, m.p. 192—193°, of Me ester), which when distilled (13 mm.) gives H_2O and a neutral oil, b.p. 200—210°, is stable to NaOBr at 0°, but at 28° gives an oil

which is freed from Br by treatment with NaOH–H_2O–Zn at 100°, affording *β-teresantalylpropionic acid*, $C_{13}H_{20}O_2$ (*Ag* salt; *Me* ester, b.p. 140—145°/19 mm.). (V) is hydrogenated (Pd on norit) to the *H_2-acid*, which is converted at 160—180° into *dihydro-α-santalylacetic acid*, b.p. 208—210°/15 mm. [*α-aminoanthraquinonyl* derivative, m.p. 105—106° (sinters 94°)]. This with HBr–AcOH in a sealed tube at 100° affords *bromotetrahydrosantalylacetic acid*, which is reduced (Na–EtOH) to *tetrahydrosantalylacetic acid* (VII), b.p. 210—213°/16 mm. (p-*bromophenacyl*, m.p. 52—53°, and *diphenacyl* derivative, m.p. 61—62°), considered to be as shown. Pure (II) has b.p.



(VII.)

177—178°/17 mm., α_{5461} −87·1° (*allophanate*, m.p. 159—160°). The strychnine salt of the H phthalate forms mixed crystals with the corresponding salts of (I). (II) with O_3 gave CH_2O and $CH_2Ac{\cdot}OH$. The following derivatives of (II) were prepared in a similar manner to those of (I): *β-santalyl chloride*, b.p. 161°/20 mm.; *β-santalylmalonic acid*, m.p. 99—101° (*Et_2* ester, b.p. 219—220°/15 mm.) (with O_3 gave CH_2O). This acid was hydrogenated in EtOH solution at 50—60° and 3 atm. giving tetrahydro-β-santalylacetic acid identical with (VII). Therefore the constitution of (II) is as shown. Although (V) is an apparently



(II.)

homogeneous cryst. solid, the products of oxidation by $KMnO_4$ and by O_3 show that the ethylenic linking in the side chain is mobile, either under the action of reagents or merely on dissolution. This is regarded as tautomerism (cf. A., 1932, 144, 1111).

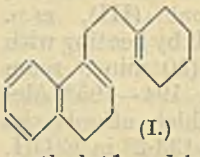
H. G. M.

Terpene compounds. I. Synthetical investigations in the cadinene group. J. C. Bardhan and S. K. Banerji (J.C.S., 1935, 476—479).—Et Δ^3-tetrahydro-*p*-toluate (I) (improved prep.), $CN{\cdot}CH_2{\cdot}CO_2Et$, and Na give *Et* 1-*carbethoxy*-4-*methyl*cyclo*hexane*-2-α-(*α-cyanoglutarate*), b.p. 198°/2 mm., hydrolysed to the -*α-glutarate*, b.p. 168°/2 mm. Cyclisation (Na–C_6H_6) and hydrolysis of this ester affords 1-*keto*-6-*methyldecalin*-4-*carboxylic acid*, m.p. 191° (*semicarbazone*, m.p. 216°), the *Et* ester, b.p. 142°/3 mm. (*semicarbazone*, m.p. 192°; *oxime*, m.p. 160°), of which with MgMeI gives a neutral product, dehydrogenated (Se) to cadalene, and an acidic product in small yield. (I) and $CN{\cdot}CHNa{\cdot}CO_2Et$ form *Et* 1-*carbethoxy*-4-*methyl*cyclo*hexane*-2-α-*cyanosuccinate* (II), b.p. 215°/7 mm., hydrolysed to -2-*succinate*, b.p. 165—167°/2 mm., which is cyclised to *Et* 7-*methyl*-[0 : 3 : 4-dicyclo]*nonan*-2-*one*-3 : 4-*dicarboxylate*, b.p. 186°/7 mm. [*semicarbazone* of acid, m.p. 221—222° (decomp.)], or followed by MeI to *Et* 3 : 7-*dimethyl*-[0 : 3 : 4-dicyclo]*nonan*-2-*one*-3 : 4-*dicarboxylate*, b.p. 175°/8 mm. (II) and $CHMeBr{\cdot}CO_2Et$ afford *Et* 1-*carbethoxy*-4-*methyl*cyclo*hexane*-2-(*α-cyano-α′-methylsuccinate*), b.p. 208°/8 mm., hydrolysed to -2-*α′-methylsuccinate*, b.p. 175°/7 mm. F. R. S.

Caryophyllenes. II. G. R. Ramage and J. L. Simonsen (J.C.S., 1935, 532—535).—During the purification of dehydronorcaryophyllenic acid (I) an optically inactive *acid*, $C_8H_{12}O_4$, m.p. 148—149°, has been isolated. Oxidation of (I) with O_3 gives α′-keto-αα-dimethylglutaric acid (2 : 4-*dinitrophenylhydrazones* A (+0·5EtOH), decomp. 243°, B (+0·5EtOH), decomp. 215—217°, and C (+4·5H_2O), m.p. 132°; p-*nitrophenylhydrazone*, decomp. 192°; *phenylsemicarbazone*, decomp. 165°, which is oxidised (H_2O_2) to *as*-dimethylsuccinic acid. (I) is probably $CMe_2{\cdot}C{\cdot}CO_2H$ / $CH_2{-}C{\cdot}CO_2H$. Bromocaryophyllenic acid is converted (Ag_2O) into the OH-acid, which is oxidised (PbO_2 followed by $KMnO_4$) to *d-cis*-norcaryophyllenic acid. Caryophyllenic acid is probably $CMe_2{\cdot}CH{\cdot}CO_2H$ / $CH_2{-}CH{\cdot}CH_2{\cdot}CO_2H$. Hippuric acid and Ac_2O–NaOAc give 2-*phenyl*-4-iso*propylideneoxazolone*, m.p. 99—100°, which with KOH followed by HCl forms α-*benzamido*-ββ-*dimethylacrylic acid*, decomp. 217°, and with HCl yields dimethylpyruvic acid (*phenylsemicarbazone*, m.p. 137°; p-*nitrophenylhydrazone*, m.p. 155°; 2 : 4-*dinitrophenylhydrazone*, m.p. 194—195°).

F. R. S.

Synthesis of polyterpenoid compounds. I. J. W. Cook and A. Dansi (J.C.S., 1935, 500—502).—Et Δ^1-*cyclo*hexenylacetate and Na in EtOH give β-Δ^1-cyclo*hexenylethyl alcohol*, b.p. 85—90°/8 mm. (3 : 5-*dinitrobenzoate*, m.p. 80°), which forms the corresponding *bromide*, b.p. 90°/7 mm. The Grignard compound with *cyclo*hexanone gives β-Δ^1-cyclo*hexenylethyl*cyclo*hexanol*, b.p. 89—91°/0·3 mm., dehydrated to a substance, b.p. 97—98°/4—5 mm., and with α-tetralone forms a carbinol, b.p. 140—175°/6 mm., dehydrated to a hydrocarbon (I), dehydrogenated (Se) to chrysene. Reduction (Na–Hg) of Et α-4-(methyl-Δ^1-*cyclo*hexenyl)propionate yields β-(4-methyl-Δ^1-*cyclo*hexenyl)-*n*-propyl alcohol, b.p. 105—109°/10 mm. (3 : 5-*dinitrobenzoate*, m.p. 71°; *bromide*, b.p. 95—100°/10 mm.). F. R. S.


(I.)

ω-Hydroxymethylfurfuraldehyde ether. K. Aso (J. Agric. Chem. Soc. Japan, 1934, **10**, 1201—1203).—Di-2 : 2′-furfuryl ether 5 : 5′-dialdehyde (I) (*phenylhydrazone*, m.p. 145°; *anilide*, m.p. 125°; *oxime*, m.p. 175°) is obtained from agar-agar, starch, sucrose (II), glucose, and fructose by heating (autoclave). (I) also accompanies 5-aldehydofurfuryl alcohol when prepared from (II). Ch. Abs. (*r*)

Action of organo-magnesium compounds on α-phenyl-β-2-furylacrylonitrile. N. Maxim and G. Aldea (Bull. Soc. chim., 1935, [v], **2**, 582—591).—α-Phenyl-β-2-furylacrylonitrile reacts with the appropriate MgRX to give saturated nitriles

C_4H_3O·CHR·CHPh·CN, whence the corresponding acids are obtained. Thus are prepared : α-*phenyl*-β-2-*furyl-valeronitrile*, b.p. 181°/18 mm., and -*valeric acid*, m.p. 93° (*chloride*, b.p. 167°/18 mm. ; *amide*, m.p. 136°; *Et* ester, b.p. 180°/22 mm.), -n-*hexonitrile*, b.p. 191°/23 mm., and -n-*hexoic acid*, m.p. 124° (*chloride*, b.p. 174—175°/18 mm. ; *amide*, m.p. 164°; *Et* ester, b.p. 184°/18 mm.), -δ-*methyl*-n-*hexonitrile*, b.p. 187°/19 mm., and -δ-*methyl*-n-*hexoic acid*, m.p. 107° (*chloride*, b.p. 185°/25 mm. ; *amide*, m.p. 132°; *Et* ester, b.p. 184—185°/18 mm.), and αβ-*diphenyl*-β-2-*furyl-propionitrile*, b.p. 225°/15 mm., and -*propionic acid*, m.p. 172° (*chloride*, b.p. 210°/14 mm. ; *amide*, m.p. 179°; *Et* ester, b.p. 213°/10 mm.). J. W. B.

α-Phenyl-β-2-furylacrylic acid and its derivatives. N. Maxim and N. Stancovici (Bull. Soc. chim., 1935, [v], **2**, 600—605).—The following derivatives of α-phenyl-β-2-furylacrylic acid (Rohmer, A., 1898, i, 300, modified) are prepared by usual methods : *chloride*, b.p. 183°/15 mm., m.p. 43°; *Me*, m.p. 88°, *Et*, m.p. 54°, *Pr*$^{\alpha}$, b.p. 187°/17 mm., *Bu*$^{\alpha}$, b.p. 204°/17 mm., and n-C_5H_{11}, b.p. 210°/17 mm., esters; *amide*, m.p. 127°; *diethylamide*, b.p. 211°/17 mm. ; *anilide*, b.p. 255°/11 mm., m.p. 104°; *methyl*-, b.p. 234°/17 mm., and *ethyl-anilide*, b.p. 236°/18 mm. ; *dimethyl*-, b.p. 205°/16 mm., and *diphenyl-amide*, b.p. 272°/12 mm., m.p. 108°. J. W. B.

Geometrical inversion in the acids derived from coumarins. B. B. Dey, R. H. R. Rao, and T. S. Seshadri (J. Indian Chem. Soc., 1935, **12**, 140—141).—Corrections and further experimental details to previous work (this vol., 211) are given. J. W. B.

Dimethyldiphenylene oxide and its oxidation product. Y. Sugii and H. Shindo (J. Pharm. Soc. Japan, 1934, **54**, 829—844).—3-Iodo-2-methoxytoluene (I) heated with Cu yields 2 : 2′-*dimethoxy*-3 : 3′-*dimethyldiphenyl*, m.p. 61°; this with HI affords 2 : 2′-*dihydroxy*-3 : 3′-*dimethyldiphenyl*, m.p. 89° (*diacetate*, an oil; *dibenzoate*, m.p. 147°), which with either $ZnCl_2$ or HBr gives 1 : 8-*dimethyldiphenylene oxide*, m.p. 89°. 2-Nitro-3-hydroxytoluene (*acetate*, m.p. 58°) is converted into 2-*amino*-3-*methoxytoluene*, b.p. 96°/4 mm. (*benzoate*, m.p. 136°), and then into 2-*iodo*-3-*methoxytoluene*, m.p. 49°, b.p. 99°/1 mm. ; this, treated similarly to (I), yields 2 : 2′-*dimethoxy*-, m.p. 124°, and 2 : 2′-*dihydroxy*-6 : 6′-*dimethyldiphenyl*, m.p. 164° (*diacetate*, m.p. 87°; *dibenzoate*, m.p. 136°), and 4 : 5-*dimethyldiphenylene oxide*, m.p. 62°. In a similar manner, 4-nitro-3-methoxytoluene is converted into 4-*amino*-, b.p. 93—94°/3 mm., and 4-*iodo*-3-*methoxytoluene*, b.p. 101°/1·5 mm. ; 2 : 2′-*dimethoxy*-, m.p. 122°, and 2 : 2′-*dihydroxy*-4 : 4′-*dimethyldiphenyl*, m.p. 120° (*diacetate*, an oil; *dibenzoate*, m.p. 148°), and 2 : 7-dimethyldiphenylene oxide (II), m.p. 80—81°. Oxidation of (II) yields 7-*carboxy*-2-*methyldiphenylene oxide*, m.p. > 280°, decarboxylated to 2-*methyldiphenylene oxide*, m.p. 65°. More drastic oxidation of (II) affords 2 : 7-*dicarboxydiphenylene oxide* (*Me*$_2$ ester, m.p. 245°), decarboxylated to diphenylene oxide. Ch. Abs. (*r*)

Transformation of *d*-catechin into cyanidin chloride. H. Appel and R. Robinson (J.C.S., 1935, 426—429).—Br in technical (not pure) dioxan and *d*-catechin Me_4 or Me_5 ether give *bromocyanidin Me*$_4$ *ether bromide*, which with PhOH–I–P gives cyanidin iodide and thence the chloride. F. R. S.

Constitution of fustin. I. Constitution of the wood of *Rhus succedanea*, L. Non-glucoside nature of fustin. II, III. Constitution of hazeic acid. IV. Constitution of fustin and synthesis of methylfustin. T. Oyamada (J. Chem. Soc. Japan, 1934, **55**, 755—762, 763—774, 775—785, 785—790).—I. Extraction with EtOAc yields fisetin and fustin (I). (I) gives neither pentoses nor hexoses with H_2SO_4.

II, III. (I) with CH_2N_2 affords *methylfustin* (II), m.p. 142—143°, which with alkali gives 7 : 3′ : 4′-trimethoxy-3-hydroxyflavone and *trimethylhazeic acid* (III), m.p. 138°. This latter with CH_2N_2 yields the *Me* ester (IV), m.p. 171—172°, of *tetramethylhazeic acid* (V), m.p. 188—190°. (IV) and (V) are also obtained directly from (I) with Me_2SO_4. (III) with acids affords *anhydrotrimethylhazeolactone*, $C_{18}H_{16}O_5$, m.p. 185°, which gives *anhydrotrimethylhazeic acid* (VI) on prolonged heating with alkali. (VI) with CH_2N_2 yields the *Me* ester, m.p. 116°, of *anhydrotetramethylhazeic acid*, m.p. 166—168° [also by fusion of (V)]. (V) with $KMnO_4$ affords a *ketone*, m.p. 98·5—99·5°, the *oxime* (VII), m.p. 134—136°, of which is converted by PCl_5 into an *amide*, m.p. 120—122°, hydrolysed to a homoveratric acid, m.p. 96—98°, and (?) 2 : 4-dimethoxyaniline, m.p. 36—38°. Hazeic acid is therefore 2 : 4-dihydroxybenzyl-3 : 4-dihydroxyphenylglycollic acid.

IV. 2-Acetoxy-3′ : 4 : 4′-trimethoxychalkone is converted into the *dibromide*, m.p. 122—124°, and thence into the *diacetate*, m.p. 133—134°; this undergoes ring-closure with HCl, yielding (II), m.p. 142—143°. (I) is thus dihydrofisetin. Ch. Abs. (*r*)

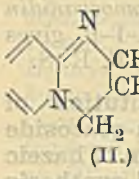
Action of sodium sulphide on polymethylene halides and the formation of "polythiophans." R. W. Bost and M. W. Conn (J. Elisha Mitchell Sci. Soc., 1934, **50**, 182—188).—The formation and physical and chemical properties of polymerides of thiophan [tetrahydrothiophen] are described. The m.p. of $(C_3H_6S)_6$, $(C_5H_{10}S)_5$, $(C_5H_{10}SO)_5$, and $(C_6H_{12}S)_4$ are 51°, 66°, 220° (decomp.), and 68°, respectively. Vigorous reduction gives H_2S and a hydrocarbon, but no mercaptan. Ch. Abs. (*e*)

Reduction of pyridine to piperidine in presence of nickel. M. I. Uschakov, S. S. Lifschitz, and N. V. Jdanova (Bull. Soc. chim., 1935, [v], **2**, 573—576).—C_5H_5N is readily reduced to piperidine, without the formation of any by-products, by H_2 and a Ni–0·4%Pd–SiO_2 gel (or Ni–Co) catalyst (I) at 130—150°. When fatigued, (I) is reactivated by addition of H_2O at 150—450°, and subsequent reduction at 450°. J. W. B.

Effect of unipolar substituents on the critical energy and probability factors in the interaction of benzyl bromide with pyridine and α-picoline. —See this vol., 710.

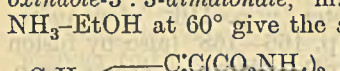
Condensation of aliphatic oxides with 2-aminopyridine. I. Knunjanz (Compt. rend. Acad. Sci.

U.R.S.S., 1935, 1, 501—506).—2-Aminopyridine (I) condenses with dry $(CH_2)_2O$ in MeOH at room temp. to give 2-*imino*-1-β-*hydroxyethyl*-1:2-*dihydropyridine*, b.p. 184—185°/17 mm., m.p. 112—113°, hydrolysed to the corresponding 2-*keto*-compound, b.p. 185°/9 mm., m.p. 100°. (I), therefore, probably reacts as 2-imino-1:2-dihydropyridine. With epichlorohydrin (I) gives the *hydrochloride*, m.p. 190°, of substance (II) [*platinichloride*, m.p. 215° (decomp.); oily *base*]. J. W. B.


(II.)

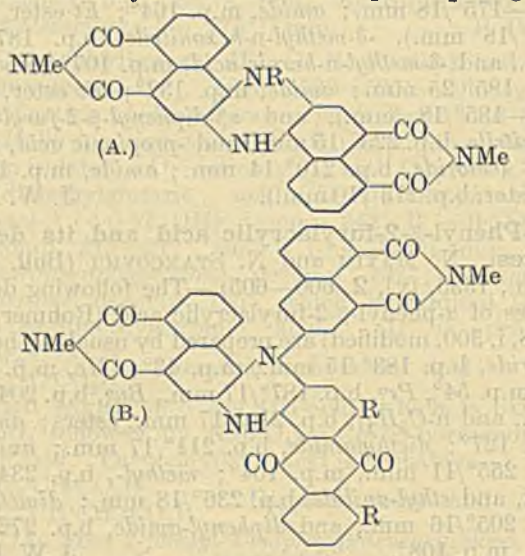
Manufacture of therapeutic agents.—See B., 1935, 430.

Condensation reactions of cyclic ketones. III. Oxindole-malonic acid derivatives. H. G. Lindwall and A. J. Hill (J. Amer. Chem. Soc., 1935, **57**, 735—737; cf. A., 1930, 480).—Isatin (I) and $CH_2(CO{\cdot}NH_2)_2$ or $CH_2(CO{\cdot}NHPh)_2$ in 3% NH_3–EtOH at 70° give 3-*diformamido*-, m.p. 245°, and 3-*diformanilido-methyleneoxindole*, m.p. 320°. $CH_2(CO_2Et)_2$ and a little $NHEt_2$ in EtOH at room temp. give *Et*$_4$ *oxindole*-3:3-*dimalonate*, m.p. 152°. (I) and 10% NH_3–EtOH at 60° give the *salt* (II), giving with HCl at room temp. 2-hydroxycinchoninic acid (III), with HCl–EtOH the Et ester of (III), with red P and HI at 140° 2-keto-1:2:3:4-tetrahydrocinchoninic acid; the *Ag*$_2$ salt with H_2SO_4 gives (III) and 1 mol. of CO_2, but with H_2S at 40° a *substance*, m.p. about 122°, which with warm H_2O_2 yields (I). R. S. C.


(II.)

[**Preparation of**] **isatin derivatives.**—See B., 1935, 444.

Derivatives of naphthalomethylimide. E. M. Francis and J. L. Simonsen (J.C.S., 1935, 496—499).—Naphthalomethylimide (I) and HNO_3 in boiling AcOH give 3-*nitronaphthalomethylimide*. (II), m.p. 226—228°, also obtained from the *imide*, m.p. 308°, sinters 305°, of 3-nitronaphthalic anhydride with Me_2SO_4 and K_2CO_3. (II) in boiling aq. EtOH with $NaHSO_3$ yields 3-*aminonaphthalomethylimide* (III), m.p. 278—280° (*azo*-β-*naphthol*, m.p. 315—317°, and *Ac*, m.p. 329—330°, derivative), the diazonium derivative of which with aq. H_2SO_4 and $(\cdot CHCl_2)_2$ yields 3-*hydroxynaphthalomethylimide* (IV), m.p. 272—273°, and 3-*chloronaphthalomethylimide*, m.p. 182—183°. 1-Chloroanthraquinone (V) and its 5- (VI) and 4- (VII) -benzamido-derivatives heated with (III), $CuCl_2$, and NaOAc in amyl alcohol give respectively 3:1-*anthraquinonylaminonaphthalomethylimide*, m.p. 286—287°, and its 5-, m.p. 338—339°, and 4-, m.p. 330—331°, -*benzamido*-derivatives, but in $PhNO_2$ at 200—210° (7 hr.) (V) yield anthraquinone with a *compound*, $C_{26}H_{16}O_4N_4$, regarded as the dihydroazine (A; R=H), whilst (VI) and (VII) give respectively a red *compound*, $C_{26}H_{16}O_4N_4$ (VIII), m.p. 331—333°, and a purple *compound*, $C_{26}H_{16}O_4N$ (IX), m.p. 320—323°, together with 1-benzamidoanthraquinone. (VIII) and (IX) are regarded as either (A; R=4- or 5-benzamidoanthraquinonyl) or (B; R=H or NHBz). Nitration of (I) with HNO_3 in boiling Ac_2O gives 3:6-*dinitronaphthalomethylimide*, m.p. 280°, also obtained from 3:6-dinitronaphthalic anhydride and dil. aq. NH_2Me, and reduced by $NaHSO_3$ to 3:6-*diaminonaphthalomethylimide*, m.p. > 400° (*Ac*$_2$, decomp. 383—384°, and 4-*benzamidoanthraquinonyl* derivative, m.p. 295—297°, sinters 280°). 4-Benzoylnaphthalic anhydride with dil. aq. NH_2Me gives


(A.)

(B.)

4-*benzoylnaphthalomethylimide*, m.p. 190—191°. Fusion of (IV) with KOH at 230° (2 hr.) gives an insol. phenol which with Na_2CO_3 and Me_2SO_4 in $PhNO_2$ yields the α-*di-imide* of 1:7-(or 1:12-)*dimethoxyperylene*-3:4:9:10-*tetracarboxylic acid*, m.p. > 400°, a purple vat dye, which in conc. H_2SO_4 is oxidised with MnO_2 in presence of H_3BO_3 to a phenol, methylated as above to the isomeric β-*di-imide*, m.p. > 400°, a red vat dye. F. R. G.

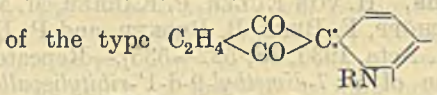
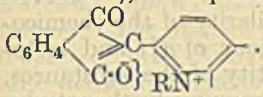
Reactions of 4-hydroxy-2-methylquinoline. A. Meyer and (Mlle.) M. Maurin (Compt. rend., 1935, **200**, 931—933).—4-Hydroxy-2-methylquinoline (I) does not condense with aromatic aldehydes (II), but N^V salts (III) of (I) heated with (II) in C_5H_5N yield styrylquinolines; (III) also condense with *p*-nitrosoamines to form *p*-aminoanilquinolines (cf. A., 1926, 1153). When treated with alkalis, (III) yield *iso*cyanines. E. W. W.

Synthesis of quinoline derivatives. A. Giacalone (Gazzetta, 1935, **65**, 124—128).—*p*-$C_6H_4Me{\cdot}NH_2$ heated with AcCl, Ac_2O, and $ZnCl_2$ gives 2-(2′-*amino*-m-*tolyl*)-4:6-*dimethylquinoline*, m.p. 252—253° (*hydrochloride*, decomp. 290°; *aurichloride*; *Ac* derivative, m.p. 286°; β-*naphtholazo*-derivative, m.p. 202—203°). E. W. W.

[**Manufacture of**] **6:7-diethoxy-1-(3′:4′-diethoxybenzyl)*iso*quinoline.**—See B., 1935, 382.

Production of 6:7-dialkoxy-1-3′:4′:5′-trialkyloxyphenyl*iso*quinolines. [Spasmolytics.]—See B., 1935, 478.

Constitution of the phthalones. R. Kuhn and F. Bär (Annalen, 1935, **516**, 155—161).—The K derivative of quinophthalone (I) (Eibner *et al.*, A., 1902, i, 644) with Me_2SO_4 in xylene at 150° affords its N-*Me* derivative (II), m.p. 249·5° (corr.), oxidised by dil. HNO_3 to *o*-$C_6H_4(CO_2H)_2$ (III) and *N*-methyl-

α-quinolone. Similar methylation of pyrophthalone (IV) affords an N-*Me* derivative (V), $+2H_2O$ and anhyd., m.p. 165° (corr.) (*perchlorate*, m.p. 179°) [also obtained in 30% yield by the action of CH_2N_2–Et_2O on (IV)], similarly oxidised to (III) and *N*-methyl-α-pyridone. The similarity of the absorption spectra of (I) and (II) and of (IV) and (V) shows that all have structures of the type  (R= H or Me), in equilibrium with the betaine forms  . J. W. B.

Tautomerism of the products of condensation of aromatic aldehydes with barbituric acid. M. Krakowski (Arch. Chem. Farm., 1935, **2**, 164—170).—The products of condensation of barbituric acid with *vanillin*, m.p. 263—270° (decomp.), and with *bourbonal*, m.p. 270° (decomp.), change colour when treated with aq. NaOH, owing to a quinonoid rearrangement; this is not possible in the cases of the compounds with *piperonal*, decomp. 200°, and with *veratraldehyde*, decomp. 270°. R. T.

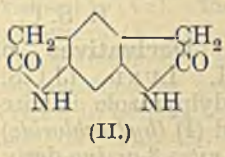
4(5)-β-Alkylaminoethylglyoxalines. B. Garforth and F. L. Pyman (J.C.S., 1935, 489—492).—*Et* α-*amino*-γ-*phenoxybutyrate hydrochloride*, m.p. 210°, is obtained from the corresponding Br-derivative (improved prep.). Reduction of α-aminobutyrolactone hydrobromide (Na–Hg) followed by NH_4CNS gives 4(5)-β-*hydroxyethyl*-2-*thiolglyoxaline*, m.p. 193°, oxidised (HNO_3) to 4(5)-β-*hydroxyethylglyoxaline* (I), m.p. 92° (*picrate*, m.p. 144°). Esterification and reduction of α-amino-γ-phenoxybutyric acid, followed by NH_4CNS, affords 4(5)-β-*phenoxyethyl*-2-*thiolglyoxaline*, m.p. 172°, oxidised (HNO_3) to 4(5)-β-*phenoxyethylglyoxaline hydrochloride*, m.p. 136—137°, which could not be satisfactorily dephenoxylated. (I) and $SOCl_2$ yield 4(5)-*chloroethylglyoxaline hydrochloride*, m.p. 126°, which with the appropriate amine affords 4(5)-β-*methylaminoethylglyoxaline dipicrate* ($+H_2O$), m.p. 188°, *dihydrochloride*, m.p. 176—177°, and *dihydrobromide*, m.p. 167°; 4(5)-β-*dimethylaminoethylglyoxaline dipicrate*, m.p. 233°, and *dihydrochloride*, m.p. 188°; 4(5)-β-*trimethylaminoethylglyoxaline dipicrate*, m.p. 212°, and *chloride hydrochloride*, m.p. 229°; 4(5)-β-*ethylaminoglyoxaline dipicrate* ($+2H_2O$), m.p. 186°, and *dihydrochloride*, m.p. 169°; and 4(5)-β-aminoethylglyoxaline (histamine). Fargher and Pyman (J.C.S., 1921, **119**, 734) did not obtain 4(5)-β-methylaminoethylglyoxaline by decarboxylation of *dl*-methylhistidine. F. R. S.

Products of oxidation of 5-αβγδ-tetrahydroxybutyl-(*d*-arabino)glyoxaline with nitric acid. J. Parrod (Compt. rend., 1935, **200**, 1049—1051).—Glucose with HNO_3 (*d* 1·38) at 100° gives 5-glyoxalylglyoxylic acid (*K* salt; *nitrate*), a little *glyoxaline*-5-*carboxylic acid*, and the *nitrate* of the lactone of γ-5-glyoxaline-αβγ-trihydroxy-(*d*-arabino)butyric acid ($+H_2O$, m.p. 104°). J. L. D.

Synthesis of 2 : 2′-dipyridyl from pyridine and ferric chloride and dipyridyl complex salts. F. Hein and H. Schwedler (Ber., 1935, **68**, [*B*], 681—684; cf. A., 1928, 1262).—The optimal conditions for the prep. of 2 : 2′-dipyridyl (I), m.p. 71—72°, consist in heating C_5H_5N and $FeCl_3$ (mol. ratio, 2·5 : 1) for 4 hr. at 330°±10°. (I) is determined by pptn. as the complex salt with $HgBr_2$. The *compounds* $[(C_5H_4N{\cdot}NC_5H_4)_2Ag]NO_3$ and $[(C_5H_4N{\cdot}NC_5H_4)_2Ag]S_2O_8,H_2O$, are described. H. W.

Complex salts of 2 : 2′-dipyridyl with zinc and cadmium.—See this vol., 714.

Indoles and isatogens. XVII. Benzodipyrroles. II. Two oxindoles of the benzodipyrrole series. P. Ruggli, B. B. Bussemaker, and W. Müller (Helv. Chim. Acta, 1935, **18**, 613—623; cf. A., 1933, 285).—Et_2 *m*-phenylenediacetate (prep. from *m*-xylene described) is converted by conc. H_2SO_4 and HNO_3 (*d* 1·52) into Et_2 4 : 6-dinitrophenylene-1 : 3-diacetate, which is smoothly reduced (H_2, Ni, EtOH) to *Et*$_2$ 4 : 6-*diaminophenylene*-1 : 3-*diacetate* (I), m.p. 68° (*picrate*, m.p. 135°; *Ac*$_2$ derivative, m.p. 187°). (I) with boiling 10% HCl affords 2 : 6-diketotetrahydro-*lin*-*m*-benzodipyrrole (II) [2 : 6-dihydroxy-*m*-α-benzbispyrrole of Davies *et al.* (J.C.S., 1922, **121**, 2652)], which darkens at 255° and becomes charred at 300°; the *Ac*$_2$ derivative has m.p. about 295° (Berl). Et_2 *p*-phenylenediacetate, conc. H_2SO_4, and HNO_3 (*d* 1·52) afford *Et*$_2$ 2-*nitrophenylene*-1 : 4-*diacetate*, m.p. 49·5° (96% yield), catalytically reduced to *Et*$_2$ 2-*aminophenylene*-1 : 4-*diacetate* (III), m.p. 46·5° [*picrate*; *Ac* derivative (IV), m.p. 95·5°]. *Oxindolyl*-6-*acetic acid*, m.p. 250°, is obtained by the action of boiling 10% HCl on (III) or of boiling conc. HCl on (IV). Addition of (IV) to conc. HNO_3 at −5° yields *Et*$_2$ 5-*nitro*-2-*acetamidophenylene*-1 : 4-*diacetate*, m.p. 118°, reduced (Ni) to *Et*$_2$ 5-*amino*-2-*acetamidophenylene*-1 : 4-*diacetate* (V), m.p. 142° [*Et*$_2$ 2 : 5-*diacetamidophenylene*-1 : 4-*diacetate* (V), m.p. 234°]. Treatment of (IV) or (V) with boiling conc. HCl yields 2 : 6-*diketotetrahydro*-lin-p-*benzodipyrrole* (VI), decomp. about 285—290°. H. W.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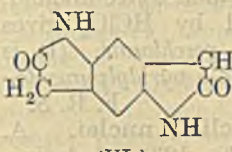
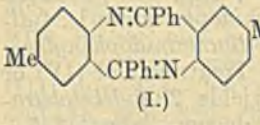

(VI.)

Pyrimidines. CXLV. Alkamine ethers of the pyrimidine and quinazoline series. J. L. Donleavy and M. A. Krise (J. Amer. Chem. Soc., 1935, **57**, 753—754; cf. this vol., 358).—The prep. of 2 : 4-dihydroxy-6-methylpyrimidine, m.p. 270—280° (decomp.), is modified. The following *pyrimidine* derivatives are prepared from the Cl-compounds and Na aminoalkoxides: 2 : 4-*di*-β-*diethylaminoethoxy*- (I), m.p. 190—191°, 2 : 4-*di*-β-*diethyl*- (II) and -*dibutylaminoethoxy*-6-*methyl*-, m.p. 198—201° and 227—230°, respectively, 4-β-*diethylaminoethoxy*-6-*methyl*- (III), m.p. 146°, and 4-γ-*diethylaminopropoxy*-6-*methyl*- (IV), m.p. 125—127°. 2 : 4-*Di*-β-*diethylaminoethoxyquinazoline*, m.p. 209—210°, is also prepared. (I)—(IV) have no local anæsthetic action and are irritant and somewhat toxic to mice when injected subcutaneously. R. S. C.

Quinazolines. XXXIX. Synthesis of quinazoline derivatives structurally analogous to the angostura alkaloids, galiopine and galipine. (Miss) E. B. Marr and M. T. Bogert (J. Amer. Chem. Soc., 1935, **57**, 729—732).—Hydrogenation (PtO_2; 96% EtOH; 29 lb. per sq. in.; 26°) of pure quinazoline gives 3 : 4-dihydroquinazoline [*hydrochloride*, m.p. 231—234°; picrate, m.p. 219—220° (corr.) (lit. about 215°)]. 2-β-*Phenylethyl*-4-*quinazolone*, m.p. 209·5—210·5° (corr.), is prepared by hydrogenation (above conditions; poor yield) or Na–Hg reduction of 2-styryl-4-quinazolone and by treating N-β-*phenylpropionylanthranilic acid*, m.p. 138·7—139·7° (corr.), first with Ac_2O and then with hot aq. NH_3; with PCl_3 and $POCl_3$ it gives 4-*chloro*-2-*phenylethylquinazoline* (50%), which with NaOMe affords 4-*methoxy*-2-*phenylethylquinazoline*, m.p. 58·5—59·5° (corr.). 2-3 : 4-*Dimethoxystyryl*-4-*quinazolone*, m.p. 268—269° (corr.) (prep. without solvent), is reduced (Na–Hg) to 2-*homoveratryl*-4-*quinazolone*, m.p. 209—210° (corr.), converted into 4-*chloro*-, m.p. 116—118°, and thence into 4-*methoxy*-2-*homoveratrylquinazoline*, m.p. 96·3—97·3° (corr.). R. S. C.

Pyridylnitropyrazole. II. Derivatives of 4-nitro-5-pyridylpyrazole. H. Lund (J.C.S., 1935, 418—420).—3-Nitro-5-pyridylpyrazole is nitrated to the 3 : 4-*dinitro*-compound (I) (*hydrochloride*), which is reduced (H_2S) to the 4-*nitro*-3-*amino*-derivative (*hydrochloride*). The amine forms the *diazonium nitrate* and *perchlorate*, and the chloride is deaminated to 4-nitro-5-pyridylpyrazole. (I) is reduced ($SnCl_2$) to 4-*nitro*-3-*hydroxylamino*-5-*pyridylpyrazole*, decomp. 177—178°, which with O_2 gives the -3-*azoxy*-compound, and with HCl–$KBrO_3$ followed by $HClO_4$ gives 4-*nitro*-3-*nitroso*-5-*pyridylpyrazole perchlorate*. (I) is reduced ($NaHSO_3$) to 3 : 4-*diamino*-5-*pyridylpyrazole*. F. R. S.

Eight-membered heterocyclic nuclei. A. Giacalone (Gazzetta, 1935, **65**, 120—123).—2-*Amino*-5-*methylbenzophenone hydrochloride*, m.p. 179—180°, when heated yields (I), m.p. 197—198°. The hydrochloride of anthranilic acid when heated yields NH_2Ph,HCl; that of the Me or Et ester dissociates, losing HCl.



(I.)

E. W. W.

[Di- and tri-pyridyl compounds of] rarer elements.—See this vol., 716.

Preparation of trimethylenetrinitroamine. G. Sollazzo (Boll. Chim. farm., 1935, **74**, 221—224, 227—228).—An improved yield (cf. A., 1933, 150) is obtained by treating dry, finely-powdered $(CH_2)_6N_4$ with 99% HNO_3 (*d* 1·52), for 12 hr. at < 10°. At −45° the yield is no greater, but the reaction is much smoother and safer. Results under other conditions are described. E. W. W.

Degradation of flavins by light. P. Karrer and H. F. Meerwein (Helv. Chim. Acta, 1935, **18**, 480—482).—*o*-$C_6H_4Cl{\cdot}NO_2$ and β-aminopropane-αγ-diol in boiling C_5H_5N give *o*-*nitro*-αγ-*dihydroxy*-β-iso*propylaniline*, reduced (Pt–H_2–EtOH) and then condensed with alloxan to 9-αγ-*dihydroxy*-β-iso*propyl*-iso*alloxazine* (I), decomp. 261—263°. In neutral aq. or aq.-MeOH solution (I) is very rapidly degraded by light with production of some alloxazine (II). In alkaline solution degradation occurs still more readily but the formation of (II) could not be established. H. W.

Synthesis of lactoflavin (vitamin-B_2) and other flavins. H. von Euler, P. Karrer, M. Malmberg, K. Schöpp, F. Benz, B. Becker, and P. Frei (Helv. Chim. Acta, 1935, **18**, 522—535).—Repeated crystallisation of 6 : 7-*dimethyl*-9-d-1′-*ribityl*iso*alloxazine* (I) has removed the discrepancy in m.p. observed previously. The complete similarity of the chemicophysical and biological behaviour of (I) and lactoflavin (II) establishes the identity of the substances. The antipellagra action of each requires further study. The products of lower biological activity observed in (II) are regarded as impurities. Other synthetic flavins are biologically inactive or have little effect. The B_2 action depends on the nature of the sugar side-chain.

Catalytic reduction (Pd) of *d*-ribose and 3-amino-4-carbethoxyamino-*o*-xylene gives 2-*carbethoxyamino*-4 : 5-*dimethylphenyl*-d-*ribamine*, m.p. 170°, $[\alpha]_D^{20}$ −13·0° ±2° in H_2O, hydrolysed and condensed with alloxan in dil. HCl to (I), m.p. 282°, $[\alpha]_D^{20}$ −92·6°±7° in 0·05*N*-NaOH (*tetra-acetate*, m.p. 238—239°). The following compounds are obtained analogously: 6 : 7-*dimethyl*-9-d-1′-*xylityl*iso*alloxazine*, m.p. 278—280°, $[\alpha]_D^{20}$ −82·2°±7° in 0·05*N*-NaOH (*tetra-acetate*, m.p. 216°); 2-*carbethoxyamino*-4 : 5-*dimethylphenyl*-l-*rhamnamine*, m.p. 183°, 6 : 7-*dimethyl*-9-l-1′-*rhamnityl*iso*alloxazine*, m.p. 269—270°, $[\alpha]_D^{20}$ −51·9°±6° in 0·05*N*-NaOH (*tetra-acetate*, m.p. 224°), and (?) 2-*hydroxy*-5 : 6-*dimethyl*-1-l-*rhamnitylbenziminazole*, m.p. 219—220°; 6 : 7-*dimethyl*-9-l-1′-*arabityl*iso*alloxazine tetra-acetate*, m.p. 215°; 2-*carbethoxyamino*-5-*methylphenyl*-d-*galactamine*, m.p. 139°, and 7-*methyl*-9-d-1′-*dulcityl*iso*alloxazine*, m.p. 239°, $[\alpha]_{644}^{20}$ −30·6°± 6° in 0·05*N*-NaOH (*penta-acetate*, m.p. 222° after softening at 150°); 2-*carbethoxyamino*-5-*methylphenyl*-l-*arabamine*, m.p. 170°, and 7-*methyl*-9-l-1′-*arabityl*iso-*alloxazine*, m.p. 284°, $[\alpha]_{644}^{20}$ −46·3°±6° in 0·05*N*-NaOH; 2-*carbethoxyamino*-5-*methylphenyl*-d-*glucamine*, m.p. 137—138°, $[\alpha]_D^{20}$ −12·2°±2° in H_2O, and 7-*methyl*-9-d-1′-*sorbityl*iso*alloxazine* (*penta-acetate*); 2-*carbethoxyamino*-5-*methylphenyl*-d-*mannamine*, m.p. 168—169°, $[\alpha]_D^{20}$ +26·7°±3° in H_2O, and 7-*methyl*-9-d-1′-*mannityl*iso*alloxazine*, m.p. 272° (*penta-acetate*, m.p. 199°). H. W.

Sugar-like side-chain of lactoflavin. R. Kuhn, H. Rudy, and F. Weygand (Ber., 1935, **68**, [*B*], 625—634; cf. A., 1934, 1460).—The hypothesis that lactoflavin (I) contains a tetrahydroxy-*n*-butyl chain is strengthened by the isolation of a *di*iso*propylidene* derivative (II), m.p. 293° (corr., decomp.), $[\alpha]_D^{20}$ +117·5° in $CHCl_3$+10% of EtOH. (II) like the corresponding tetra-acetate is freely sol. in $CHCl_3$, from which it is not removed by H_2O. It is readily hydrolysed by dil. AcOH to (I). The absorption spectra of (I) and (II) are nearly identical. iso*Propylidenelactoflavin* has m.p. 277° (corr., decomp.). Treatment of (I) with $Pb(OAc)_4$ yields 6 : 7-dimethylalloxazine, identified by transformation by CH_2N_2 into 1 : 3 : 6 : 7-tetramethylalloxazine, m.p. 250°

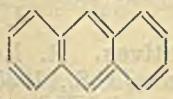
(corr.); it is assumed that 6 : 7-dimethylflavin-9-acetaldehyde is intermediately produced and then undergoes alloxazine fission even more readily than the corresponding -9-acetic acid. Crystallisation of (I) from various media shows that the m.p. of the most sol. fraction (III) can be raised to 293°, but elementary composition and $[\alpha]_D$ remain unchanged from (III) to the most sparingly sol. portions (IV). (I) of m.p. 271° and 293°, respectively, yield the same Ac_4 derivative, m.p. 243°. Probably within these limits the temp. of decomp. is influenced by traces of impurity and the m.p. may possibly be raised further. The marked dependence of $[\alpha]_D$ on concn. in 0·05*N*- or 0·1*N*-NaOH is the same for all fractions and marked differences between $[\alpha]_D$ of (III) and (IV) are not observed in the strongly dextrorotatory solutions containing $Na_2B_4O_7$ in which $[\alpha]_D$ is nearly independent of concn. The fractionations do not entirely preclude the presence of other flavins but are not in harmony with the views of Karrer *et al.* (cf. this vol., 359).

4 : 5-Dinitro-*o*-xylene is condensed with *l*-arabinamine in 80% EtOH at 135° to 4-*nitro*-5-l-*arabityl-amino*-o-*xylene* (V), m.p. 216°, $[\alpha]_D^{20}$ −1°±1° in C_5H_5N, the absorption spectrum of which very closely resembles that of 4-nitro-5-methylamino-*o*-xylene. (V) and alloxan in boiling dil. HCl give 6 : 7-*dimethyl*-9-l-*araboflavin* (VI), m.p. 294—295° (decomp.), $[\alpha]_D^{21\cdot5}$ −80·4±10° in 0·1*N*-NaOH, $[\alpha]_D^{21\cdot5}$ +367°±10° in presence of $Na_2B_4O_7$, $[\alpha]_{Cd}^{21\cdot6}$ +220°±10° in presence of $Na_2B_4O_7$. The m.p. is not influenced by the presence of (I) of differing origin. The half-periods of photolysis of (I) and (VI) are almost identical. Nevertheless, the identity of (I) and (VI) is not regarded as established since the m.p. of the Ac_4 derivative of (VI) could not be raised above 217° by repeated chromatographic analysis whereas the Ac_4 derivative of (I) has m.p. 243°, and the biological activity of (VI) is at least 3 times > that of (I). Reduction (H_2–PtO_2) of (V) and treatment of the product with alloxan in boiling dil. AcOH leads to 4-*alloxanylamino*-5-l-*arabitylamino*-o-*xylene*,

$CO<^{NH\cdot CO}_{NH\cdot CO}>C{:}N\cdot C_6H_2Me_2{:}NH\cdot CH_2\cdot[CH\cdot OH]_3\cdot CH_2\cdot OH$

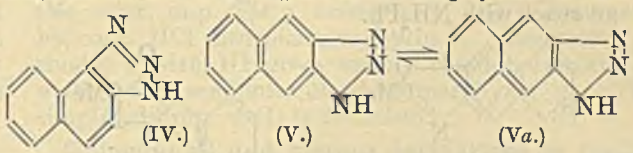
m.p. 216° (decomp.), and (VI). H. W.

Tricyclic compounds in which naphthalene is allied to a heterocyclic component. K. Fries, R. Walter, and K. Schilling (Annalen, 1935, **516**, 248—285).—Re-determinations show that the heat of combustion of anthracene (I) is 7 kg.-cal. > that of phenanthrene (II), in accordance with the view that the latter is the more stable compound. For (I) the

(1*a*.)  (1*b*.)

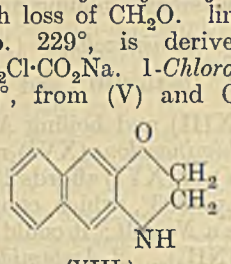
constitution I*a* is preferred to 1*b* since 2 : 6-dihydroxyanthracene is converted by Br in dioxan into 1 : 5-*dibromo*-2 : 6-*dihydroxyanthracene*, decomp. 135°; the Me_2 *ether*, m.p. 280° (decomp.) after blackening at 275° (obtained with CH_2N_2), is oxidised by CrO_3 in AcOH to 1 : 5-*dibromo*-2 : 6-*dimethoxyanthraquinone* (III), decomp. 345°. (III) is synthesised by the action of P_2O_5 on 2-*bromo*-3-*methoxybenzoic acid*, m.p. 154° (2-*amino*-3-*methoxybenzoic acid*, m.p. 167°).

In *ang*-naphthatriazole (IV) in contrast with *lin*-naphthatriazole (V) no part of the ring system is in a

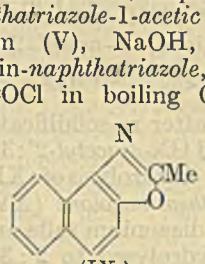


(IV.) (V.) (V*a*.)

state of strain, in accordance with which it has the lower heat of combustion. (IV) is markedly less saturated than (V) as shown by the relative ease of hydrogenation and chemical behaviour which differ as do those of (I) and (II). Hydrogenation of (V) by Na–Hg in boiling EtOH leads to 8 : 9-*dihydro*-lin-*naphthatriazole*, m.p. 157° (1-*Me*, m.p. 147°, and 1-*Ac*, m.p. 173°, derivatives), oxidised by $Na_2Cr_2O_7$ and dil. H_2SO_4 to lin-*naphthatriazole*-8 : 9-*quinone* (VI), m.p. 241° (1-*acetyl*-, m.p. 149°, and 1-*methyl*-, m.p. 175°, -lin-*naphthatriazole* are described). Catalytic hydrogenation of (V) (Pt-sponge in AcOH) of (V) gives 4 : 5 : 6 : 7-*tetrahydro*-lin-*naphthatriazole* (VII), m.p. 162° (1-*Ac*, m.p. 114°, and 1-*Me*, m.p. 99°, derivatives), oxidised to (VI). Partial hydrogenation of (V) gives a mixture of (V) and (VII). Under similar conditions hydrogenation of (IV) is scarcely appreciable. (VII), also obtained by oxidation of (V), is stable towards NH_2Ph in boiling EtOH. It gives a 1-*Ac*, m.p. 186°, and 1-*Me*, m.p. 237°, derivative. It is converted by Zn dust in boiling Ac_2O into the Ac_3 derivative, m.p. 165°, of 8 : 9-dihydroxy-*lin*-naphthatriazole. Chlorination of (V) in AcOH gives 8 : 9-*dichloro*-lin-*naphthatriazole*, m.p. 291° (decomp.), oxidised to (VI); attempts to obtain an additive product or to introduce 1Cl were unsuccessful. Br in AcOH at room temp. transforms (V), apparently through a very unstable dibromide, into 9-*bromo*-lin-*naphthatriazole*, m.p. 244° (decomp.), whereas a larger proportion of halogen gives 8 : 9-*dibromo*-lin-*naphthatriazole*, m.p. 278° (decomp.), oxidised to (VI). (V) and CH_2O in EtOH afford 1-*hydroxymethyl*-lin-*naphthatriazole*, m.p. 191° with loss of CH_2O. lin-*Naphthatriazole*-1-*acetic acid*, m.p. 229°, is derived from (V), NaOH, and $CH_2Cl\cdot CO_2Na$. 1-*Chloroacetyl*-lin-*naphthatriazole*, m.p. 179°, from (V) and $CH_2Cl\cdot COCl$ in boiling C_6H_6,



(VIII.)

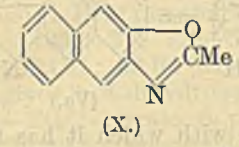


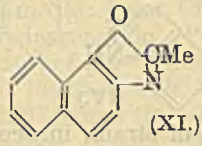
(IX.)

is transformed by $AlCl_3$ in $PhNO_2$ into lin-*naphthamorpholone* (VIII), m.p. 270°, also obtained from 2 : 3-$NH_2\cdot C_{10}H_6\cdot OH$ and $CH_2Cl\cdot CO_2H$.

2 : 3-$C_{10}H_6(NH_2)_2$ is transformed by boiling HCO_2H into lin-*naphthiminazole*, m.p. 221° (1-*Ac* derivative, m.p. 172°), which is not reduced by Na–Hg or catalytically. It is oxidised by $Na_2Cr_2O_7$ and boiling dil. H_2SO_4 to lin-*naphthiminazole*-8 : 9-*quinone*, m.p. > 400° after blackening at 320°, which does not react with NH_2Ph, gives a 1-*Me* derivative, m.p. 286°, with NaOH and Me_2SO_4 and is reduced by Zn dust and boiling Ac_2O to the Ac_3 derivative, m.p. 216°, of 8 : 9-dihydroxy-*lin*-naphthiminazole. 2-*Methyl*-lin-*naphthiminazole*, m.p. 286°, from 2 : 3-$C_{10}H_6(NH_2)_2$ and AcOH

is oxidised to 2-*methyl*-lin-*naphthiminazole*-8 : 9-*quinone*, m.p. > 350° after blackening at 330°, which does not react with NH_2Ph.

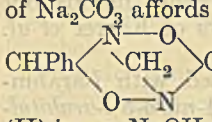

(X.)

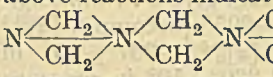

(XI.)

2-Methyl-2′ : 1′-naphthoxazole (IX), b.p. 312°/760 mm., is best obtained by heating 1 : 2-$NH_2{\cdot}C_{10}H_6{\cdot}OH$ with Ac_2O and distillation of the product under atm. pressure; the Ac_3 derivative of 1 : 2-$NH_2{\cdot}C_{10}H_6{\cdot}OH$ has m.p. 119·5°. In a similar manner, 2 : 1-$NH_2{\cdot}C_{10}H_6{\cdot}OH$ affords 2-*methyl*-1′ : 2′-*naphthoxazole* (X), m.p. 41·5°, b.p. 302°. 3-*Acetamido*-2-*naphthyl acetate*, m.p. 188°, passes at 258° into 2-*methyl*-2′ : 3′-*naphthoxazole* (XI), m.p. 87·5°, b.p. 310°/760 mm. The heats of combustion of (IX) and (X) are approx. equal when allowance is not made for the latent heat of fusion of (IX) and the behaviour of (IX), (X), and (XI) towards conc. acid clearly shows (X) to be the most labile compound.

2 : 3-$NH_2{\cdot}C_{10}H_6{\cdot}CO_2H$ is transformed by boiling Ac_2O into *dehydro*-2-*acetamido*-3-*naphthoic acid* (XII), $C_{10}H_6{<}^{NH{\cdot}CMe}_{CO-O}$, m.p. 171° or, after re-solidification, m.p. 173°, converted by hot AcOH into 2 : 3-$NHAc{\cdot}C_{10}H_6{\cdot}CO_2H$, m.p. 248° (decomp.), which reforms (XII) with boiling Ac_2O. (XII) and N_2H_4,H_2O in EtOH yield 2-*acetamido*-3-*naphthohydrazide* (XIII), m.p. 225° (decomp.; bath pre-heated to 220°), which is not hydrolysed by HCl–EtOH. 2-*Amino*-3-*naphthohydrazide*, m.p. 206—210° (decomp.; bath 200°), is obtained from 2 : 3-$NH_2{\cdot}C_{10}H_6{\cdot}CO_2Me$ or, preferably, *lin*-benzoisatoic anhydride and N_2H_4,H_2O. 2-*Acetamido*-3-*naphthoazide*, m.p. 233°, from (XIII) and $NaNO_2$ in dil. HCl, passes when heated in C_6H_6 into N-*acetyl*-2′ : 3′-*naphthiminazolone* (XIV), $C_{10}H_6{<}^{NAc}_{NH}{>}CO$, m.p. 238°, whereas in boiling AcOH it gives 2-*acetyl*-2′ : 3′-*naphthiminazolone* (XV), $C_{10}H_6{<}^{N}_{NH}{>}C{\cdot}OAc$, m.p. 248° (bath 240°) and m.p. 260° after re-solidification. (XIII) and boiling Ac_2O afford ON-*diacetyl*-2′ : 3′-*naphthiminazolone* (XVI), m.p. 258°. Hydrolysis of (XIV), (XV), or (XVI) affords 2′ : 3′-*naphthiminazolone* (XVII), m.p. 393°, which couples with diazonium salts and gives a *Na* salt; it could not be hydrolysed to 2 : 3-$C_{10}H_6(NH_2)_2$. 2-*Acetamido*-3-*naphthoamide*, m.p. 240° (decomp.), most easily prepared from (XII) and conc. NH_3, is transformed by the Hofmann degradation into (XVII) and by partial hydrolysis with dil. HCl into 2-*amino*-3-*naphthoamide* (XVIII), m.p. 233° (bath 230°). Diazotisation and subsequent heating of (XVIII) leads to 4-*hydroxy*-lin-*naphtha*-1 : 2 : 3-*triazole*, $C_{10}H_6{<}^{N{=}{=}N}_{C(OH){:}N}$, decomp. 250°. H. W.

Structure of hexamethylenetetramine. M. Dominikiewicz (Arch. Chem. Farm., 1935, **2**, 78—129).—$(CH_2)_6N_4$ (I) and Ac_2O in Et_2O yield $CH_2\left(N{<}^{CH_2}_{CH_2}{>}NAc\right)_2$ (II), m.p. 186—187°, and $NAc_2{\cdot}CH_2{\cdot}N{<}^{CH_2}_{CH_2}{>}NAc$, whilst with BzCl and aq. NaOH the products are $NR{<}^{CH_2}_{CH_2}{>}NBz$ (III), m.p. 218—219°, $NR{<}^{CH_2}_{CH_2}{>}NR$, m.p. 267—268° (R = $NBz_2{\cdot}CH_2{\cdot}$), and $NH{<}^{CH_2}_{CH_2}{>}N(OBz){<}^{CH_2}_{CH_2}{>}NH{<}^{CH_2}_{CH_2}{>}N{\cdot}OBz$, m.p. 187—188°; benzoylation in $CHCl_3$–C_5H_5N yields the *products* $NBz{<}^{CH_2}_{CH_2}{>}NR'{<}^{CH_2}_{CH_2}{>}NBz{<}^{CH}_{CH}{>}NR'$ (R′ = C_5H_5NCl), m.p. indefinite, $NCl{<}^{CH_2}_{CH_2}{>}N{<}^{CH_2}_{CH_2}{>}N{<}^{CH_2}_{CH_2}{>}NBz$, m.p. 189—190°, $NR{<}^{CH_2}_{CH_2}{>}N{\cdot}CH_2{\cdot}NHBz$, m.p. 235—236°, and $CH_2(NHBz)_2$, whilst benzoylation in $CHCl_3$ in presence of Na_2CO_3 affords (III) and

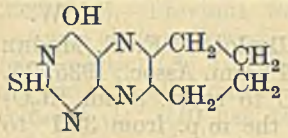

, m.p. 127—128°. BzCl and (II) in aq. NaOH yield $NBzAc{\cdot}CH_2{\cdot}N{<}^{CH_2}_{CH_2}{>}N{\cdot}CH_2{\cdot}NBzAc$, m.p. 256°. The above reactions indicate that (I) is


R. T.

Miscellaneous observations. H. Biltz and (in part) H. Rakett, H. Krzikalla, M. Heyn, H. E. Edlefsen, P. Damm, L. Loewe, and H. Pardon (J. pr. Chem., 1935, [ii], **142**, 193—200).—With 33% aq. NH_2Me polyglycollide and $NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CBr_3$ afford, respectively, *glycolmethylamide*, b.p. 161—165°/9—11 mm., sinters 62°, m.p. 72°, and *tribromoacetmethylamide*, m.p. 144—146°. Barbituric acid and $H_2C_2O_4$ heated together at 150° afford dibarbituric acid (I), probably $CO{<}^{NH{\cdot}CO}_{NH{\cdot}CO}{>}CH{\cdot}C{<}^{NH{\cdot}CO}_{CH{-}CO}{>}NH$, readily purified as its *Br*$_2$-derivative, which affords (I) by reduction with $SnCl_2$–HCl. $CCl_3{\cdot}COCl$ and C_6H_6 with anhyd. $AlCl_3$ give $OH{\cdot}CPh{:}CPh_2$, but use of moist $AlCl_3$ gives $CCl_3{\cdot}COPh$. Passage of HCl into a melt of $CO(NHMe)_2$ (2 mols.) and dialuric acid (1 mol.) affords 1 : 3 : 7 : 9-tetramethyl*spiro*-5 : 5-hydantoin (A., 1911, i, 240). 5-Chloro-3 : 7-dimethyl*iso*uric acid is simply reduced by NaCN at 0° to give 3 : 7-dimethyluric acid. The action of KI–$Na_2S_2O_3$ on 5-chloro-3 : 7-di- and -1 : 3 : 7-tri-methyl*iso*uric acid (A., 1911, i, 168) affords only the normal uric acid derivatives. J. W. B.

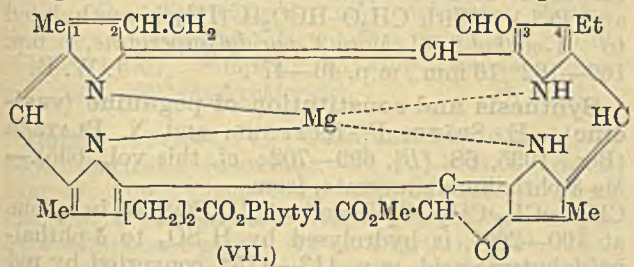
Thiopyrimidazine derivatives. R. Robinson and (Miss) M. L. Tomlinson (J.C.S., 1935, 467—470).—Thiobarbituric acid (I) and HNO_2 give *thioviolu*ric *acid*, which could not be hydrolysed. Diazotised *p*-$C_6H_4Me{\cdot}NH_2$ with (I) yields p-*tolueneazothiobarbituric acid*, and with 4-amino-2-thiouracil followed by reduction gives 4 : 5-diamino-2-thiouracil. The $(NH_2)_2$-compound with phenylglyoxal gives 7-*thiol*-9-*hydroxy*-2(or 3)-*phenylpyrimidine*, with phenanthraquinone forms *thiolhydroxyphenanthraquinone*, with *cyclo*hexanedione affords 11-*thiol*-13-*hydroxy*-

3 : 4 : 5 : 6-*tetrahydrobenzpyrimidazine* (II), and with alloxan yields *thioltrihydroxybispyrimidazine*. On oxidation of (II) in aq. solution the appearance of fluorescence corresponds rather closely with the behaviour of vitamin-B_1, but the substances are very different from the vitamin in other respects. (II) is



F. R. S.

Chlorophyll. LIV. Chlorophyll *b*. VII. Fine structure of chlorophyll *b*. H. Fischer and J. Grassl (Annalen, 1935, **517**, 1—21).—Phæophorbide *b* (I) has the same isocyclic ring as phæophorbide *a* (II) and its abnormal reactions are attributed to the presence of CHO at 3. Treatment of phæophorbide *b* monoxime (CHO stabilised by conversion into CH:N·OH) with CH_2N_2 in MeOH gives the oxime of rhodin *g* Me_3 ester, m.p. 238°. Phæophorbide *b* dioxime is merely esterified by CH_2N_2. Treatment of methylphæophorbide *b* monoxime (III) with anhyd. KOAc and boiling Ac_2O yields *pyrophæophorbide* b *nitrile*, m.p. 256°, which could not be hydrolysed to the corresponding acid. In contrast to dihydrophæophorbide *b*, methylphæophorbide *b* and $CHN_2{\cdot}CO_2Me$ give an additive *product* (IV), $C_{39}H_{40}O_8N_4$, m.p. 262°, in which the presence of CHO is shown by isolation of the *monoxime* (V), m.p. 264°, and of the isocyclic ring by that of the *dioxime*, m.p. 263°. Treatment of (III) with $CHN_2{\cdot}CO_2Me$ affords (V), hydrolysed by 20% HCl to (IV). Oxidation of (III) with CrO_3–H_2SO_4 gives ill-defined results, whereas treatment with HI (*d* 1·7) in AcOH yields a cryst. porphyrin converted by CH_2N_2 into phæoporphyrin b_6 Me ester (VI), m.p. 276° (monoxime). Oxidation of (VI) with CrO_3–H_2SO_4 gives a compound, m.p. 202°, identical with that obtained by oxidation of the adduct, m.p. 205°, of protoporphyrin and $CHN_2{\cdot}CO_2Et$ and of (II) with $CHN_2{\cdot}CO_2Et$. The formulation of the unsaturated side-chain cannot be decided definitely, but it and CHO cannot be attached to the same pyrrole nucleus, and position 2 in nucleus I is the sole available position



(VII.)

since methylethylmaleinimide is not available from intact chlorophyll *b*, which is therefore probably formulated as shown.

Reduction of phæoporphyrin b_6 (VII) (*monoxime*, m.p. > 300°, *dioxime*) [H_2–Pd–HCO_2H] leads to phæoporphyrin a_5 and 9-hydroxydeoxyphæoporphyrin a_5, transformed by warm conc. H_2SO_4 into phylloerythrin, thus accomplishing the transition from the *b* to the *a* series in a porphyrin with isocyclic ring; a similar change is accomplished with greater difficulty starting with (V). Oxidation of (VII) with I in abs. EtOH yields 10-ethoxyphæoporphyrin b_6 (Me ester, m.p. 274°; *oxime*, m.p. 283°), converted by conc. HCl into phæoporphyrin b_8. Reduction of rhodin *g* with HI gives mainly rhodinporphyrin g_6 with small amounts of rhodinporphyrin g_5. The simplified prep. of (I) is described. H. W.

Chlorophyll and hæmin derivatives in rocks, petroleums, coals, and phosphorites.—See this vol., 727.

Composition and specificity of hæmoglobins. Spectral characters and specificity of hæmoglobins.—See this vol., 640.

Benzanthrones with condensed heterocyclic rings, their derivatives, and dyestuffs derived from them. I. M. Kitajima (J. Chem. Soc. Japan, 1934, **55**, 887—895).—The prep. and properties of a no. of benzanthrone deoxy-compounds are described. Ch. Abs. (*r*)

Pyrolysis of saccharinoxime. (Sna.) A. Mannessier-Mameli (Gazzetta, 1935, **65**, 77—84).—Decomp. of saccharinoxime (I) at 208° (cf. A., 1933, 288) gives oxides of N, saccharin (II), and *ψ*-saccharinamine (III), new m.p. 315° (*Ac* derivative, m.p. 256°). The action of HNO_2 on (I) also gives (II) and (III), with a substance, m.p. 190°. Treatment of (III) with NaOH gives NH_3 and (III). E. W. W.

Action of hydroxylamine hydrochloride on oximinotriphenylpyrrole. T. Ajello (Gazzetta, 1935, **65**, 176—182).—These react to give a *substance*, $C_{22}H_{16}O_2N_2$ (I), m.p. 170—171°, reduced to $C_{22}H_{18}ON_2$, m.p. 98°, and hydrolysed (KOH–EtOH) to a *substance*, $C_{15}H_{12}ON_2$ (II). The formulæ $\overset{CPh{\cdot}CHPh{\cdot}CBz}{N\!-\!O\!-\!N}$ and $\overset{CPh{\cdot}CHPh{\cdot}CH}{N\!-\!O\!-\!N}$ are suggested for (I) and (II), respectively. E. W. W.

Dioximes. CVIII. P. Gramatieri (Gazzetta, 1935, **65**, 102—108).—When the phenylhydrazone of 3-benzoyl-5-phenyl-1 : 2 : 4-oxadiazole (I) is heated, the oxadiazole ring is opened, and a triazole ring closed, forming 5-*benzamido*-2 : 4-*diphenyl*-1 : 2 : 3-*triazole*, m.p. 190°. From this, the 5-NH_2-compound, m.p. 83—84°, and its *benzylidene* derivative, m.p. 126—127°, are prepared. The p-*bromophenylhydrazone*, m.p. 146°, of (I) similarly gives 5-*benzamido*-4-*phenyl*-2-p-*bromophenyl*-1 : 2 : 3-*triazole*, m.p. 185°. The *phenylhydrazone*, m.p. 178° (softens at 110°), of 3-p-*toluyl*-5-*phenyl*-1 : 2 : 4-*oxadiazole*, m.p. 115° (decomp.), which is obtained (HCl) from its *oxime*, m.p. 174—175°, in turn obtained (NaOH) from the *Bz* derivative, m.p. 174°, of β-amino-*p*-tolylglyoxime, similarly isomerises to 5-*benzamido*-2-*phenyl*-4-p-*tolyl*-1 : 2 : 3-*triazole*, m.p. 177—178°. E. W. W.

Thionaphthenopyrazoles. W. J. Barry and E. W. McClelland (J.C.S., 1935, 471—474).—3-Hydroxy-2-acetyl-1-thionaphthen (I) with $NHPh{\cdot}NH_2$,HCl yields 1-*phenyl*-3-*methyl*-4 : 5-*thionaphthenopyrazole* (II), m.p. 120°, oxidised to the *S*-dioxide, and with *p*-$C_6H_4Br{\cdot}NH{\cdot}NH_2$ gives 1-p-*bromophenyl*-3-*methyl*-4 : 5-*thionaphthenopyrazole*, m.p. 159°, oxidised to the *dioxide*, m.p. 207°. 3-*Hydroxy*-2-*acetyl*-1-*thionaphthen*-p-*bromophenylhydrazone*, m.p.

160—161°, and 1 : 3-*diphenyl*-4 : 5-*thionaphthenopyrazole*, m.p. 171°, are similarly oxidised to the dioxides. (I) and N_2H_4,HCl give a *bis*-compound, m.p. 305°, and 3-*methyl*-4 : 5-*thionaphthenopyrazole*, m.p. 185°, oxidised to the *dioxide*, m.p. 244—246°. Reduction (Na) of (II) affords 1 : 5-diphenyl-3-methylpyrazoline and a *product*, m.p. 122—124° (*NO*-compound, m.p. 202—203°; *Br*-compound, m.p. 142—143°), which is probably a diphenylmethylpyrazole. F. R. S.

Manufacture of heterocyclic amino-compounds.—See B., 1934, 444.

Production of compounds of the cyanine type.—See B., 1935, 398.

Alkaloids of the Chinese drug "chin-shih-hu." III. Dendrobine. H. Suzuki, I. Keimatsu, and K. Ito (J. Pharm. Soc. Japan, 1934, **54**, 802—819, 820—823).—Dendrobine (I) is now regarded as $C_{16}H_{25}O_2N$. (I), with EtOH–KOH, yields *dendrobinic acid* (II), $C_{16}H_{27}O_3N$, m.p. 227°, $[\alpha]_D^{31}$ −27·5° in EtOH [*aurichloride*, decomp. 85°; *methiodide* (III), decomp. 211°; *Me* ester (IV), m.p. 94°, $[\alpha]_D^{14\cdot5}$ −17·5° in EtOH]. (IV) forms an *aurichloride*, m.p. 169°, and an *Ac* derivative, m.p. 76° [*aurichloride*, m.p. 93—103° (decomp.)]. (II) or (IV) with H_2O_2 affords *dendrobine N-oxide*, $C_{16}H_{25}O_3N,H_2O_2$, decomp. 150°, $[\alpha]_D^{25}$ −37·76° in EtOH (*aurichloride*, decomp. 184°). (III) with moist Ag_2O yields *dendrobine methohydroxide*, decomp. 251° (*aurichlorides*, anhyd., decomp. 237—239°; $+H_2O$, decomp. 200°). (I) with CNBr yields *cyanonordendrobine*, m.p. 188°, which with dil. HCl gives *nordendrobinecarbamide* (V), $C_{15}H_{22}O_2N{\cdot}CO{\cdot}NH_2$, decomp. 240°, $[\alpha]_D^{13}$ −127·9° in EtOH (*aurichloride*, decomp. 176°). (V) yields *nordendrobinic acid* (*aurichloride*, decomp. 197°) when treated with EtOH–KOH. (V), with HNO_2, affords a *carbamic acid*, $C_{16}H_{23}O_4N$, m.p. 134°, and *nordendrobine*, m.p. 117—118° [*Ac* derivative, m.p. 114·5°, $[\alpha]_D^{17}$ −149·5° in EtOH; *NO*-derivative (VI), m.p. 172°]. (VI) is also formed from (V) with HNO_2. The alkaloids present in *Dendro flaviflorum*, *D. linawianum*, and *D. longicalcaratum* have been examined. Ch. Abs. (*r*)

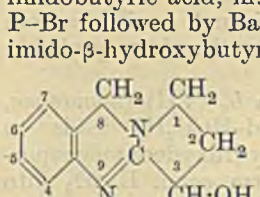
***Senecio* alkaloids. I. Alkaloids of *S. platyphyllus*, D.C.** A. Orekhov [with W. Tiedebel] (Ber., 1935, **68**, [*B*], 650—655).—The air-dried roots are moistened with 10% NH_3 and extracted with $C_2H_4Cl_2$. The extract is shaken with 3*N*-HCl, which is neutralised with 50% NaOH and treated with excess of 25% NH_3, whereby *seneciphylline* (I), $C_{17}H_{23}O_5N$, m.p. 217—218° (decomp.), $[\alpha]_D$ −128·04°, is pptd. The mother-liquors from (I) are extracted with Et_2O, whereby *platyphylline* (II), $C_{17}H_{25}O_5N$, m.p. 124—125°, $[\alpha]_D$ −45·09° in $CHCl_3$, is obtained. (II) is a moderately strong base which contains 1 OH but not OMe or NMe. N is *tert.* and probably dicyclic. It gives a *perchlorate*, m.p. 222—223° (decomp.) after becoming discoloured at 210°, *picrolonate*, m.p. 205—206° (decomp.), *aurichloride*, m.p. 200—201° (decomp.), and *methiodide*, m.p. 216—217°. It is hydrolysed by NaOH–EtOH to the monobasic *platynecic acid*, $C_{10}H_{14}O_4$, m.p. 154—155°, which contains 1 OH and platynecine, $C_7H_{11}O_2N$ [*aurichloride*, m.p. 209—210° (decomp.)]. (I) contains 1 OH, whereas OMe and NMe are absent. N is *tert.* It yields a *perchlorate*, darkens at about 220° and subsequently chars, *picrate*, m.p. 182—183°, *aurichloride*, m.p. 162—163° (decomp.), *platinichloride*, darkens at 205° and subsequently chars, and *methiodide*, m.p. 231—232° (decomp.). (I) is hydrolysed to an acid (or mixture) and an NH_2-alcohol (*aurichloride*, m.p. 163—164°). In view of the difficulties of combustion, the C_{17} formulæ are recorded with reserve. H. W.

Crystalline ephedrine alkaloid. E. E. Moore and D. L. Tabern (J. Amer. Pharm. Assoc., 1935, **24**, 211—213).—Addition of H_2O to cryst. (from Et_2O) anhyd. ephedrine (I) lowers the m.p. from 38·1° to 32·1° when a eutectic mixture of (I)–(I) hydrate containing 1·5% of H_2O is present; with further addition the m.p. rises to a max. of 40° with 5% of H_2O, corresponding to a hemihydrate. F. O. H.

Ergot alkaloids. W. A. Jacobs and L. C. Craig (Science, 1935, **81**, 256—257).—Lysergic acid (I), phenylalanine (II), and NH_3 have been obtained from ergotamine (III) and there is evidence that proline (IV) is also a constituent of (III). Neither *iso*butyrylformic acid (V) nor its reduction product could be detected in the cleavage products of (III), but $AcCO_2H$ (VI) has been detected after alkaline hydrolysis. Ergotinine and ergotoxine appear to be derivatives of (I), (II), (IV), and (V), but in (III) and in ergotaminine (V) is replaced by (VI). L. S. T.

Introduction of an amino-group into alkaloids by sodamide and potassamide. II. α-Aminoanabasine. M. I. Kabatschnik and M. M. Katznelson (Bull. Soc. chim., 1935, [v], **2**, 576—582).—Treatment of anabasine with $NaNH_2$ in $NPhMe_2$ at 135—145° affords a mixture of α- (I), m.p. 89·5—90°, and α′-aminoanabasine (II), m.p. 109° (main product), separated by fractional crystallisation from PhMe and H_2O. (I) is 2-(2′-*amino*-3′-*pyridyl*)*piperidine* [*platinichloride*, darkens 260°, not melting at 300°; *picrate*, m.p. 244·5—245° (decomp.)], a constitution erroneously assigned by Menschikov *et al.* (A., 1934, 422) to (II), which is actually 2-(6′-*amino*-3′-*pyridyl*)*piperidine*. Thus with HNO_2–HCl (I) and (II) give, respectively, α-, b.p. 126°/1·8 mm., m.p. 58·5—59·5°, and α′-*chloroanabasine* (III), m.p. 99·5—100°, oxidised by $KMnO_4$ to, respectively, 2- and 6-chloropyridine-3-carboxylic acid (also synthesised from the 6-OH-acid and PCl_5). With CH_2O–HCO_2H (III) is methylated to 1-*methyl*-2-(6′-*chloro*-3′-*pyridyl*)*piperidine*, b.p. 160—162°/16 mm., m.p. 46—47°. J. W. B.

Synthesis and constitution of peganine (vasicine). E. Späth, F. Kuffner, and N. Platzer (Ber., 1935, **68**, [*B*], 699—702; cf. this vol., 635).—Me δ-phthalimidobutyrate, from $CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Me$ and *o*-$C_6H_4(CO)_2NK$ in xylene at 190—200°, is hydrolysed by H_2SO_4 to δ-phthalimidobutyric acid, m.p. 113—115°, converted by red P–Br followed by $BaCO_3$–boiling H_2O into δ-phthalimido-β-hydroxybutyric acid (I), m.p. 147—148°.

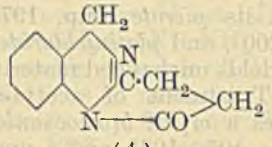


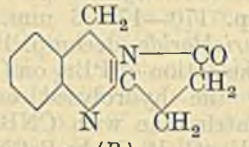
(III.)

(I) is hydrolysed (25% HCl at 100°), esterified (MeOH–HCl), and condensed with *o*-$NO_2{\cdot}C_6H_4{\cdot}CH_2Cl$ to 3-*hydroxy*-1-*o*-*nitrobenzylpyrrolid*-2-*one* (II), m.p. 150—151° (vac.), accompanied by 3-hydroxypyrrolidone, m.p. 84—85°. Reduction of (II)

by $SnCl_2$ and HCl in AcOH leads through the NH_2-compound to 3-hydroxy-Δ^9-pegene (III), m.p. 211—212° (vac.), identical with natural peganine. H. W.

Constitution of vasicine. J. N. Ray, K. S. Narang, and H. R. Juneja (Current Sci., 1935, **3**, 352—353).—Previous work on the constitution of vasicine (I) is reviewed. The picrolonates of reduced (electrolytic) (*A*) 4-hydroxy-2-propylquinazoline and 4-hydroxy-3-allylquinazoline differ from that of reduced (I). (*B*) has been synthesised but not yet reduced.


(*A*.)


(*B*.)

F. N. W.

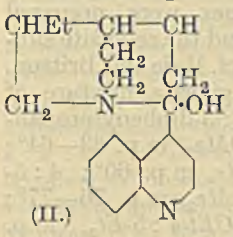
Harmine and harmaline series. II. Nitro- and amino-derivatives of harmine and harmaline. *O*-Alkyl ethers of harmol and harmalol. R. Konovalova and A. Orekhov (Arch. Pharm., 1935, **273**, 156—163; cf. A., 1934, 1236).—Harmaline (I) can be oxidised to harmine (II) by $K_2Cr_2O_7$–H_2SO_4 (cf. A., 1927, 682; 1934, 1117). (I) and (II) can be demethylated to give harmalol (III) and harmol (IV), respectively, by means of syrupy H_3PO_4 (*d* 1·7) at 120°. The following were prepared from (IV), NaOR and *p*-$C_6H_4Me{\cdot}SO_3R$ (R=requisite alkyl): *harmalol* O-*Et*, m.p. 199—200°; O-*Pr*$^{\alpha}$, m.p. 203—204°; O-*Bu*$^{\alpha}$, m.p. 218—220°; and O-iso*amyl*, m.p. 237—238°, *ethers* (cf. A., 1933, 839). The O-*Et*, m.p. 247—249°, and O-*Pr*$^{\alpha}$, m.p. 195—197°, *ethers* of (III) were prepared similarly. Nitroharmaline (V), m.p. 132° (decomp.) (lit. m.p. 122°) (improved prep.), is oxidised (CrO_3) to nitroharmine (VI) (cf. A., 1912, i, 645), which with MeI–$PhNO_2$–PhMe gives Py-N-*methylnitroharmine hydriodide*, and this with NaOH or aq. NH_3 affords the *base* (darkens at 250° and decomp. at 270°). Py-N-*Methylnitroharmaline*, m.p. 189—190° (*hydriodide*, m.p. 200—205°), is obtained in a similar manner. Reduction (Fe–HCl) of (V) gives *aminoharmaline*, m.p. 209—210° ($+1H_2O$, lost at 105°). The *hydrochloride* and unstable *dihydrochloride* are described. In solution the base is readily oxidised by air. Similarly (VI) affords *aminoharmine*, m.p. 231—232° (*hydrochloride*). H. G. M.

Indole series. V. Complete synthesis of physostigmine (eserine). P. L. Julian and J. Pikl (J. Amer. Chem. Soc., 1935, **57**, 755—757; cf. this vol., 635).—*dl*-Eserethole could not be resolved by *d*-camphorsulphonic (I) or *d*-tartaric acid. *dl*-5-Ethoxy-1 : 3-dimethyloxindolylethylmethylamine (II) (modified prep.) and (I) give usually the d-*camphorsulphonate*, m.p. 78°, of (II), or, best when appropriately seeded, the *salt*, m.p. 160°, of the *d*-amine (*picrate*, m.p. 175°), $[\alpha]_D^{28}$ +30° in EtOH; the base from the mother-liquors affords the d-*tartrate*, m.p. 175—176°, of the *l*-amine, $[\alpha]_D^{28}$ −30° in EtOH (*picrate*, m.p. 175°; *dl*-picrate, m.p. 192°), which by reactions already described yields *l*-eserethole, *l*-eseroline, and *l*-physostigmine, identical with the natural product and its derivatives. R. S. C.

Optical crystallographic data for some salts of cinchonine. C. F. Poe and C. A. Swisher (J. Amer. Chem. Soc., 1935, **57**, 748—749).—The optical properties of 13 salts of cinchonine are described. The following are new: *perchlorate*, $+H_2O$, *bromate*, $+H_2O$, o-*chlorobenzoate*, chlorate, $+H_2O$, nitrate, $+H_2O$, and iodate, $+H_2O$. R. S. C.

Stereochemical studies. III. Connexion between optical rotation and configuration of quinine alkaloids. R. Ludwiczakówna and J. Suszko (Rocz. Chem., 1935, **15**, 57—67, and Bull. Acad. Polonaise, 1934, **A**, 402—412).—The $[M]_D$–[HCl] curves of cupreidine, cinchonine chloride, deoxycinchonine, α-*iso*cinchonine, β-*iso*quinidine, *N*-benzylcinchotoxine, and cinchene in EtOH are of the same general type, showing that C atom (4), which is in cinchonine combined with a carbinol OH, does not, as stated by Emde (A., 1932, 759), determine the optical behaviour of the cinchona alkaloids; the validity of Emde's conclusions, based on optical methods, as to the configuration of these alkaloids is questioned. The above compounds exhibit max. rotation in presence of about 2 equivs. of HCl, that of cinchotoxine falls to a const. val. in presence of > 1 equiv. of HCl, whilst that of *N*-methyl-β-*iso*quinicine falls abruptly from 0 to 2 equivs., and then gradually with increasing [HCl]. R. T.

Rearrangement of hydrocinchonine by esterification in two stages. R. Ludwiczakówna and J. Suszko (Arch. Chem. Farm., 1935, **2**, 196—202).—Hydrocinchonine in C_5H_5N gives a p-*toluenesulphonyl* derivative, m.p. 166—167° (decomp.), $[\alpha]_D^{20}$ +52·5° in EtOH, converted by KOBz in EtOH (at the b.p.; 95 hr.) into the *Bz* derivative (I), m.p. 141—142°, $[\alpha]_D^{18}$ −25·5° in EtOH, of hetero*hydrocinchonine* (II), m.p. 201—202°, $[\alpha]_D^{20}$ +154·5° in EtOH, prepared by hydrolysis of (I). The structure (II) is also assigned to the product obtained analogously from cinchonine, and erroneously termed *epi*cinchonine (A., 1933, 288). R. T.


(II.)

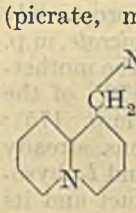
Spatial rearrangement of quinine alkaloids to *epi*-bases. J. Fiedziuszko and J. Suszko (Arch. Chem. Farm., 1935, **2**, 139—148, and Bull. Acad. Polonaise, 1934, **A**, 415—420).—Hydrocinchonidine (I) is heated at 160° with 25% HCl for 50 hr., 10% aq. $NaNO_2$ is added to complete pptn. of N-*nitrosohydrocinchotoxine* (II), m.p. 99—100°, $[\alpha]_D^{20}$ −21·0° in EtOH (*hydrochloride*, m.p. 107—108°), the solution is made alkaline and extracted with Et_2O, (I) is eliminated from the extract as tartrate, and epi*hydrocinchonidine* (III), m.p. 107—108°, $[\alpha]_D^{18}$ +46·0° in EtOH (*picrate*, an oil; *picrolonate*, m.p. 196—198°; *methiodide*, m.p. 237—238°, $[\alpha]_D^{18}$ +38·0° in H_2O; *benzoate*, m.p. 137—138°, $[\alpha]_D^{15}$ −71·0° in EtOH), is isolated from the residual solution. epi*Hydrocinchonine* (IV), m.p. 128—129°, $[\alpha]_D^{20}$ +89·0° in EtOH (*picrate*, m.p. 212—213°; *picrolonate*, an oil; *methiodide*, m.p. 231—232°, $[\alpha]_D^{20}$ +54° in H_2O; *benzoate*, m.p. 156—157°, $[\alpha]_D^{18}$ +157° in EtOH), is prepared from hydrocinchonine hydrochloride and 25% HCl (50 hr. at 160°). Hydrocinchotoxine, obtained by

heating (III) or (IV) with 25% aq. AcOH at 100° (30 hr.), yields (II) when heated with HNO_2 (cf. A., 1932, 759). R. T.

Cinchona alkaloids in pneumonia. II. Ketone formation with sodamide. (Miss) A. G. Renfrew and L. H. Cretcher (J. Amer. Chem. Soc., 1935, **57**, 738—739; cf. this vol., 636).—Dihydroquinine and cinchonine with $NaNH_2$ in hot xylene give 40 and 21% yields, respectively, of the corresponding ketones (cf. Tschitschibabin, B., 1923, 1201). Na in xylene gives very poor yields. δ-Methylpentan-β-ol and benzhydrol do not give ketones with $NaNH_2$. R. S. C.

Constitution of *apo*cinchene and synthesis of its methyl and ethyl ethers. J. Kenner and F. S. Statham (J.C.S., 1935, 299—303).—*m*-NO_2·C_6H_4·COMe is reduced [$(NH_4)_2S$] to the amine, which affords *m*-OH·C_6H_4·COMe, the *semicarbazone*, m.p. 194—196°, of which with KOH at 190° gives *m*-C_6H_4Et·OH (p-*nitrobenzoate*, m.p. 68°) (better yields than by Clemmensen's method). *m*-C_6H_4Et·OAc with $AlCl_3$ in $PhNO_2$ at 0° yields 4-*hydroxy*-2-*ethylacetophenone* (I), b.p. 150—152°/0·45 mm., m.p. 102° (*semicarbazone*, m.p. 172°; p-*nitrobenzoate*, m.p. 80°), converted by H_2O_2 into ethylquinol. (I) is reduced (Clemmensen) to 3 : 4-*diethylphenol* (II), b.p. 106°/0·5 mm. (p-*nitrobenzoate*, m.p. 81—82°; *Me ether*, b.p. 124—125°/23 mm.; *Et ether*, b.p. 120—125°/20 mm.). The *acetate* of (II), b.p. 113—115°/0·35 mm., with $AlCl_3$ at 140° gives 2-*hydroxy*-4 : 5-*diethylacetophenone*, b.p. 134—137°/0·75 mm. [*semicarbazone*, m.p. 240°; *Me ether*, m.p. 35—39° (*semicarbazone*, m.p. 128°)]. The following substituted β-chloropropiophenones were prepared from β-chloropropionyl chloride and the requisite substituted benzene and $AlCl_3$ in CS_2 [cf. Hale and Britton, A., 1919, i, 332, which method gives a mixture of β-chloropropiophenone (III) and 1 : 3-diphenylpropan-1-one in the prep. of (III)]: 4-*OMe*-, m.p. 63—64°; 4-*Me*, m.p. 80—81°; 2-*OMe*-5-*Me*, m.p. 60°; 4 : 5-Me_2, m.p. 71—72°; 2-*OMe*-4 : 5-Me_2, m.p. 76—77°; 2-*OMe*-4 : 5-Et_2, m.p. 41°; 2-*OEt*-4 : 5-Et_2, m.p. 81—82°. These ketones were converted into the corresponding substituted 4-phenylquinolines by Blaise and Maire's method (A., 1908, i, 566) for 4-alkylquinolines. The *picrates* of these substances have the following m.p.: 4-*OMe*, 232—234° (decomp.); 4-*Me*, 206° (decomp.); 2-*OMe*-5-*Me*, 213° (decomp.); 4 : 5-Me_2, 250—253°; 2-*OMe*-4 : 5-Me_2, 215° (decomp.); 2-*OMe*-4 : 5-Et_2 (IV), 200° (decomp.); 2-*OEt*-4 : 5-Et_2 (V), 180—181° (decomp.). (IV) and (V) are identical, respectively, with the picrates of the Me and Et ethers of *apo*cinchene (VI) (cf. A., 1885, 1248), and the free base from (V) was identical with the Et ether of (VI). (VI) is therefore 4-(2′-hydroxy-4′ : 5′-diethyl)quinoline. H. G. M.

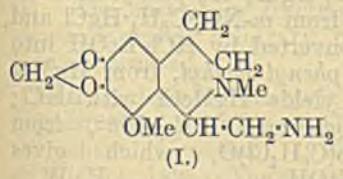
Constitution of matrine. XV. Products of the distillation of potassium matrate with soda-lime. H. Kondo, E. Ochiai, K. Tsuda, and S. Yoshida. **XVI. Dehydrogenation of matrine.** H. Kondo and K. Tsuda (Ber., 1935, **68**, [*B*], 570—581, 644—650).—XV. The basic portion of the products of the distillation of K matrate with CaO–NaOH consists essentially of matrine (I), α- (II) and β-matrinidine. An unstable fraction, b.p. 55—90°/14 mm., is also present which is catalytically hydrogenated to 1-butylpiperidine and norlupinane, thus confirming the identity of β-lupinane obtained by distillation of (I) with Zn dust. The *tert.*-N of (I) therefore belongs to the lupinane ring as with other leguminosæ alkaloids. (II) contains a double linking and is readily hydrogenated (Pd–C in AcOH) to *dihydro-α-matrinidine* $C_{12}H_{22}N_2$, b.p. 122—123°/2 mm., m.p. 66° [*hydrochloride*, decomp. > 340°; *methiodide*, decomp. 246°; *picrate*, decomp. 251°; *Bz* derivative (III), m.p. 112°, and its *platinichloride*; p-*nitrobenzoyl* compound, m.p. 136°; *Ac* derivative, b.p. 170—173°/3 mm., and its *picrate*, m.p. 197°, *aurichloride*, decomp. 199—200°, and *platinichloride*]. The action of PBr_5 on (III) yields unchanged material or the hydrolysed base. Treatment of acetyl-α-matrinidine with CNBr gives a cryst. *bromocyanide* (IV), $C_{12}H_{21}N_2Ac$,BrCN, m.p. 105—106°, and a non-cryst., probably isomeric *bromocyanide* (V) which decomposes when heated in high vac. (IV) is dehalogenated (H_2–Pd–C) and hydrolysed by conc. HCl to the corresponding sec.-*amines*, $C_{12}H_{24}N_2$ (VI), b.p. 130°/6 mm., m.p. 42—45° (*picrate*, decomp. 163—164°; *hydrobromide*, decomp. > 320°; *platinichloride*; *di*-p-*nitrobenzoate*, m.p. 240—241°), and $C_{12}H_{23}N_2Ac$ (VII), b.p. 160—162°/6 mm., m.p. 79—80° (*platinichloride*, decomp. 188—189°; *benzoate*, m.p. 135—136°; *picrate*, decomp. 163—164°). Stronger heating with conc. HCl converts (VII) into (VI). When similarly treated (V) affords two *bases*, $C_{12}H_{21}N_2$ (VIII), b.p. 126—127°/6 mm., and $C_{12}H_{24}ON_2$ (IX), b.p. 170—175°/6 mm., m.p. 128—129°. (VIII) gives a *hydrobromide*, $C_{12}H_{24}N_2$,2HBr, decomp. > 350°, *di-α-naphthylcarbamate*, decomp. 281°, and amorphous *di*-p-*nitrobenzoate*, decomp. 224—226°, whilst (IX) yields a *hydrobromide*, decomp. > 330°, and *aurichloride*, m.p. about 185° after softening at 96°. Dehydrogenation of (VI) and (VIII) is effected by 40% Pd–asbestos at 270—310° and the products are separated by KH_2PO_4 into a more strongly (X) and a more weakly (XI) basic portion. (XI) from each is $C_{12}H_{14}N_2$, b.p. 119—120°/2 mm. It gives the red Ehrlich reaction and the pine-shaving change only when impure. Although scarcely basic in character it gives a *methiodide*, m.p. 217—218° (decomp.), *picrate*, m.p. 187—188°, and *styphnate*, m.p. 178—179°. (X) from (VI) is $C_{12}H_{18}N_2$, m.p. 160—170°/4 mm., m.p. 111° (*hydrochloride*, m.p. 179°; *aurichloride*, m.p. 126°; *picrate*, m.p. 147°; *methiodide*, m.p. 166—167°). It is a *sec.-tert.*-amine of which the *tert.*-N is as weak as in the compound $C_{12}H_{14}N_2$. (X) from (VIII) is $C_{12}H_{18}N_2$, b.p. 148—150°/2 mm., m.p. 189—190° (*methiodide*, m.p. 205—206; *picrate*, m.p. 192—194°), and is identical with the product of the distillation of α-matrinidine with Zn dust. Dehydro-α-matrinidine, b.p. 178°/3 mm. (picrate, m.p. 214—215°; *styphnate*, m.p. 189°; *hydrochloride*, decomp. 282°; *aurichloride*, m.p. 139°), is obtained as by-product. Oxidation of the base $C_{12}H_{14}N_2$ with $KMnO_4$ affords quinolinic acid with small amounts of a neutral cryst. *substance*. The annexed scheme shows the fundamental skeleton of (I).



XVI. (I) is not affected by CNBr in boiling C_6H_6 or PhMe and is unchanged by H_2 under pressure in presence of PtO_2–AcOH. (I) is dehydrogenated by Pd–asbestos at 280—310° and the product is separated by KH_2PO_4 into *octadehydromatrine* (XII) $C_{15}H_{16}ON_2$, m.p. 175—177°, $[\alpha]_D$ ±0° in EtOH, and the *substance* (XIII) $C_{14}H_{20}N_2$, b.p. 138°/0·001 mm. (XII) gives a violet pine-shaving reaction and reddish-violet Ehrlich test; it is indifferent towards CH_2N_2, resembling 2-pyridone in these respects. It dissolves in dil. HCl. $AuCl_3$ and $PtCl_4$ are immediately reduced and $KMnO_4$ is slowly decolorised. A methiodide or acyl derivatives could not be obtained. It does not react with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ or *p*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$. It is stable towards KOH–EtOH or molten KOH. (XIII) is a monacidic, *tert.*-amine, giving a *hydrochloride*, m.p. 208°, *aurichloride*, m.p. 118°, *methiodide*, m.p. 129°, and *picrate*, m.p. 142°. Since it does not yield NO- or Ac derivatives, the second N is probably *tert.* It probably contains 2 double linkings but is very resistant towards catalytic hydrogenation (PtO_2) under pressure. Under these conditions, (XII) is reduced to *didehydromatrine* (XIV), $C_{15}H_{12}ON_2$, m.p. 103°. (XIV) does not give a reaction with $FeCl_3$ or the Ehrlich test and is unaffected by KOH–EtOH. It forms a weakly basic *NO*-derivative. The *hydrochloride*, m.p. 171°, non-cryst. *methiodide* (identified as the *aurichloride*, m.p. 96°, of the corresponding methochloride), and *picrate*, m.p. 147°, are described. (XIV) in Et_2O is converted by BzCl–NaOH into the *Bz* derivative, m.p. 70° (*hydrochloride*, m.p. 223°); the p-$NO_2{\cdot}C_6H_4{\cdot}CO$ compound has m.p. 98°.

H. W.

Derivatives of 1-methylanhydrocotarnine. O. J. Magidson and I. E. Gorbovizki (Ber., 1935, 68, [*B*], 656—664).—Nitromethylanhydrocotarnine (Hope *et al.*, J.C.S., 1911, 99, 2114) is reduced by $SnCl_2$ and HCl at 28—30° to 1-*aminomethylanhydrocotarnine* (I), m.p. 183° (decomp.) [*picrate*, m.p. 150—151° (decomp.); *hydrochloride*, m.p. 170° (decomp.); *Ac* derivative, m.p. 155—160°].



(I.)

Condensation of (I) with the requisite aldehyde and hydrogenation (PtO_2) of the Schiff's bases leads to the following *-aminomethylanhydrocotarnines*: *benzylidene-*, m.p. 150°; non-cryst. *benzyl-* (hygroscopic *dihydrochloride*, m.p. 172—173° or m.p. 181—183° in sealed capillary); *veratrylidene-*, m.p. 140—141°; 3′ : 4′-dimethoxybenzyl- [*dihydrochloride* (+H_2O), m.p. 184°]; *vanillylidene-*, m.p. 192°; non-cryst. *vanillyl-* (*dihydrochloride*, m.p. 131° in sealed tube); *piperonylidene-*, m.p. 161—162°; non-cryst. *piperonyl-* (*dihydrochloride*, m.p. 178·5—180·5°); 3′ : 4′-*dihydroxybenzylidene-*, m.p. 192°; 3′ : 4′-dihydroxybenzyl- (*dihydrochloride*); *furfurylidene*, m.p. 154—155°; 4′-*hydroxybenzylidene-*, m.p. 180—181°; 4′-hydroxybenzyl- [dihydrochloride (+2H_2O), m.p. 91—93°]; 4′-*methoxybenzylidene-*, m.p. 153—154°; 4′-methoxybenzyl- (*dihydrochloride*, m.p. 196—197°); 2′-*hydroxybenzylidene-*, m.p. 145—146°; 2′-hydroxybenzyl- (*dihydrochloride*, m.p. 200°). *p*-$C_6H_4Me{\cdot}NH_2$ is converted by $NEt_2{\cdot}CH_2{\cdot}CH_2Cl$,HCl at 100° into β-*diethylaminoethyl*-p-*toluidine*, b.p. 136—140°/6 mm., which with cotarnine and NaOEt in EtOH at 40—50° yields 4′-β-*diethylaminoethylaminobenzylanhydrocotarnine* (very hygroscopic *trihydrochloride*; *platinichloride*, $C_{25}H_{35}O_3N_3,H_2PtCl_6$, m.p. 165°). *Anhydrocotarnino*-p-*acetamidotoluene* (cf. Ahluwalia *et al.*, A., 1932, 1047) has m.p. 121—125°. The physiological behaviour of the compounds is fully described.

H. W.

New synthesis of 3 : 11-dimethoxyoxyprotoberberine, and syntheses of 2 : 3-methylenedioxy-11 : 12-dimethoxyoxyprotoberberine and 2 : 3 : 11 : 12-tetramethoxyoxyprotoberberine. S. N. Chakravarti and M. Swaminathan (J.C.S., 1935, 293—295).—5-Methoxyhomophthalic acid and β-*m*-methoxyphenylethylamine at 180° yield 5-*methoxyhomophthalo*-β-m-*methoxyphenylethylimide*, m.p. 133°, hydrolysed to 5-*methoxyhomophthalo*-β-m-*methoxyphenylethylamic acid*, m.p. 167°, the *Me* ester, m.p. 85°, of which with $POCl_3$ yields 3 : 11-dimethoxyoxyprotoberberine (A., 1927, 1096). Therefore, in the conversion (*loc. cit.*) of formyl-6-methoxy-1-(3′-methoxybenzyl)-1 : 2 : 3 : 4-tetrahydro*iso*quinoline into 3 : 11-dimethoxydihydroprotoberberine, ring-closure takes place *para* to the 3′-OMe; the constitution of dimethoxytetrahydroprotoberberine is not thereby fully determined. In a similar way, 5 : 6-dimethoxyhomophthalic acid (I) and β-piperonylethylamine at 180° give 5 : 6-*dimethoxyhomophthalo*-β-*piperonylethylimide*, m.p. 223°, hydrolysed to 5 : 6-*dimethoxyhomophthalo*-β-*piperonylethylamic acid*, m.p. 245°, the *Me* ester, m.p. 169—170°, of which with $POCl_3$ yields 11 : 12-dimethoxy-2 : 3-methylenedioxyoxyprotoberberine, m.p. and mixed m.p. 230—231° (A., 1934, 669). Also, (I) and β-veratrylethylamine at 180° give 5 : 6-*dimethoxyhomophthalo*-β-*veratrylethylimide*, m.p. 180°, hydrolysed to the *amic acid*, m.p. 165°, the *Me* ester, m.p. 123°, of which with $POCl_3$ yields 2 : 3 : 11 : 12-*tetramethoxyoxyprotoberberine* (II), m.p. 190—191°. 2 : 3 : 11 : 12-Tetramethoxytetrahydroprotoberberine is converted by I in EtOH +NaOAc into 2 : 3 : 11 : 12-*tetramethoxyprotoberberinium iodide* (III), m.p. 245° [chloride (IV), m.p. 225°, from (III) and AgCl]. (IV) and aq. KOH afford (II).

H. G. M.

Tetraphenylarsonium halides. F. F. Blicke and E. Monroe (J. Amer. Chem. Soc., 1935, 57, 720—722).—$AsPh_3O$ with MgMeBr gives triphenylmethylarsonium bromide and with MgPhBr or MgPhI *tetraphenylarsonium bromide* (I), m.p. 273—275° (with 2Br gives a *tribromide*, m.p. 215—216°), and *iodide* (I), m.p. 312—313° (with 2I gives a *tri-iodide*, m.p. 228—230°). (I) and HCl give the *chloride* (III), m.p. 256—257° (*compound* with 1HCl, cryst.). (I) or (III) with HI or NaI give (II). MgPhBr with $AsPh_2Cl_3$ or $AsPh_3Cl_2$ gives $AsPh_3$ and Ph_2, but with $AsPhO_2$ affords some (I). (I) behaves as a strong electrolyte, but in an attempt to prepare $AsPh_4$ a little $AsPh_4Cl_3$ only was obtained. (III) has no trypanocidal action and no germicidal action against *S. hæmolyticus*, but is germicidal against *S. aureus* at 1 : 600.

R. S. C.

Phenyl- and diphenyl-arsines. F. F. Blicke and J. F. Oneto (J. Amer. Chem. Soc., 1935, 57, 749—753; cf. A., 1933, 518).—The following reactions were effected in N_2. AsPhCl·OMe and AsH_2Ph in C_6H_6 give $(AsPh)_2$. AsH_2Ph and CPh_3Cl give

$AsPh(CPh_3)_2$ and HCl, which react further to give $AsPhCl_2$ and $CHPh_3$. $AsHPh_2$ (I) and $CH_2Cl{\cdot}CO_2H$ (II) at 160° give AcOH and $AsPh_2Cl$, which with more (I) gives $(AsPh_2)_2$ (III), m.p. 129—131°; this with more (II) yields $AsPh_2Cl$ (modified prep. from $AsHPh_2$ and $CH_2Cl{\cdot}COCl$; 65% yield). MgPhBr and (I) give $AsPh_2{\cdot}MgBr$, which with $HgCl_2$ affords first (III) and then $AsPh_2Cl$, with $AsCl_3$, I, or $AsPh_2I$ gives (III), with $(m\text{-}NO_2{\cdot}C_6H_4)_2AsI$, m.p. 113—115° (lit. 112°), yields $[(m\text{-}NO_2{\cdot}C_6H_4)_2As]_2$, with $CHPh_2Br$ gives $(CHPh_2)_2$ and (III), with CPh_2Cl_2 gives (III) and $(CPh_2{:})_2$, with $o\text{-}C_6H_4(CH_2Br)_2$ gives *ωω-di(diphenylarsino)-o-xylene* (IV), m.p. 104—105° (*$HgCl_2$*-compound, m.p. 220—221°), with $COPh_2$ gives $(CPh_2{\cdot}OH)_2$, and with CPh_3Br gives a mixture containing CPh_3, which with HCl affords $CHPh_3$ and $AsPh_2Cl$. $AsPh_2Cl$ is unaffected by HCl in presence of CPh_3, but (III) and CPh_3 with HCl give $AsPh_2Cl$ and $CHPh_3$; it is believed that an equilibrium, $(III)+2CPh_3 \rightleftharpoons 2AsPh_2{\cdot}CPh_3$, exists. $AsPh_2{\cdot}MgBr$ and CPh_3 with (not without) H_2O give (I), which then reacts with the CPh_3 to form (III) and $CHPh_3$. (IV) slowly absorbs O_2 in solution and with I gives $AsPh_2I$ and $o\text{-}C_6H_4(CH_2I)_2$. The prep. of bromo-, *iodo-*, m.p. 94—95°, and *hydroxy-*, m.p. 156—157°, unimol. in (CH_2Br_2), *-diphenylarsine* is described. R. S. C.

Conversion of 3-nitro-4-methylphenylarsinic acid into 3-amino-4-carboxyphenylarsinic acid by intramolecular dismutation, and the action of hydrobromic acid on *m*-arsanilic acid and 3-amino-4-carboxyphenylarsinic acid. A. H. C. P. Gillieson, W. O. Kermack, and W. T. Spragg (J.C.S., 1935, 470—471).—3-Nitro-4-methylphenylarsinic acid and 30% aq. NaOH give 3-amino-4-carboxyphenylarsinic acid, which with HBr gives $p\text{-}C_6H_4Br{\cdot}NH_2$, identified as the Ac derivative. HBr and *m*-arsanilic acid form $p\text{-}C_6H_4Br{\cdot}NH_2$. The mechanism of the reaction is discussed; HBr probably causes decarboxylation. F. R. S.

New derivatives of *p*-arsanilic acid. VI. *p*-Arsinopimelanilic and *p*-arsinosuberanilic acid and related compounds. G. T. Morgan and E. Walton (J.C.S., 1935, 290—293).—With $SOCl_2$ Me H pimelate yields its *acid chloride*, b.p. 135—136°/17 mm., which with atoxyl gives *Me* p-*arsonopimelanilate* (I) (*Na* salt). The *Et* compound (II) (*Na* salt) was similarly prepared. (I) and (II) are hydrolysed to the corresponding *acid*, which with aq. SO_2–HCl–I (trace) affords crude p-*dichloroarsinopimelanilic acid*, m.p. 114—116°, hydrolysed to p-*oxyarsinopimelanilic acid*. The following *amides*, $p\text{-}AsO_3H_2{\cdot}C_6H_4{\cdot}CO{\cdot}[CH_2]_5{\cdot}CO{\cdot}NRR'$, were prepared from (I) or (II) and the corresponding amine: R,R′= *H,H* [*Na* salt $(+2H_2O)$]; *H,Me* [NH_2Me salt, *Na* salt $(+2H_2O)$]; *Me,Me* [can be prepared from (I) but not (II)] [*Na* salt $(+3H_2O)$]; *H,Et* [Na salt $(+2H_2O)$]; *H,Pr*$^{\alpha}$ [*Na* salt $(+H_2O)$]. Pimelyl dichloride and atoxyl afford *pimelanilido*-pp′-*diarsinic acid* (Na_2 salt). With $SOCl_2$, Me H suberate yields its *acid chloride*, b.p. 163—165°/34 mm., which with atoxyl gives *Me* p-*arsonosuberanilate* [*Na* salt $(+H_2O)$]. The *Et* compound (*Na* and Na_2 salts) was similarly prepared. These esters are hydrolysed to the *acid* [*Na* salt $(+H_2O)$], which affords p-*dichloroarsinosuberanilic acid*, m.p. 152—156°, hydrolysed to p-*oxyarsinosuberanilic acid*. The following *amides* $p\text{-}AsO_3H_2{\cdot}C_6H_4{\cdot}CO{\cdot}[CH_2]_6{\cdot}CO{\cdot}NRR'$ are described: R,R′=*H,H* [*Na* salt $(+2H_2O)$], *H,Me* (*Na* salt); *Me,Me* [*Na* salt $(+H_2O)$]; *H,Et* [*Na* salt $(+H_2O)$]. Suberyl dichloride with atoxyl and NaOH affords *suberanilide*-pp′-*diarsinic acid* [Na_2 salt $(+2H_2O)$]. The Na salts of these compounds have a smaller trypanocidal power than the corresponding succinic and glutaric homologues, which are the most active members in this series (cf. A., 1931, 636; 1932, 290). H. G. M.

Mesityldimethylphosphine. W. C. Davies (J.C.S., 1935, 462—464).—Mesityldichlorophosphine (I) and MgMeI give *mesityldimethylphosphine*, b.p. 133°/16 mm. (*methiodide*, m.p. 232°; *ethiodide*, m.p. 168°; additive *compound*, m.p. 58—59°, with CS_2). The rates of addition of (I) to alkyl iodides show it to be more reactive than the As analogue. F. R. S.

Synthesis of asymmetric organo-mercury compounds. R. C. Freidlina, A. N. Nesmejanov, and K. A. Kozeschkov (Ber., 1935, **68**, [*B*], 565—569).—Hot alcoholic solutions of the Hg aryl (alkyl) salt, the arylating agent (I), and aq. alkali are rapidly cooled. Apparently any organo-metallic or -metalloid compound which in the widest sense can be mercurated can function as (I). The individuality of liquid (aromatic-aliphatic) compounds which cannot be distilled without decomp. is regarded as established when they yield no distillate when heated at 100°/10—15 mm. The following changes are recorded: *Hg phenyl ethyl*, from HgEtBr, $SrPh_2Cl_2$, and NaOH, transformed by HCl into HgEtCl, m.p. 192°; *Hg methyl α-naphthyl*, m.p. 84—86°, from HgMeI and $Sn(C_{10}H_7)_2$, which gives $C_{10}H_8$ with HCl–EtOH; *Hg phenyl* p-*nitrophenyl*, m.p. 144—145° (decomp.), from $p\text{-}NO_2{\cdot}C_6H_4{\cdot}HgCl$ and $SnPh_2Cl_2$, converted by HCl–EtOH into $NO_2{\cdot}C_6H_4{\cdot}HgCl$; *Hg phenyl* m-*nitrophenyl*, m.p. 113—115°, from $m\text{-}NO_2{\cdot}C_6H_4{\cdot}HgCl$ and $SnPh_2Cl_2$ or $SnPhCl_3$, converted by HCl–EtOH into $m\text{-}NO_2{\cdot}C_6H_4{\cdot}HgCl$; *Hg phenyl methyl*, from HgMeI and $BPh(OH)_2$, which yields HgMeCl with HCl; *Hg benzyl* p-*chlorophenyl*, m.p. 104—108°, from $CH_2Ph{\cdot}HgCl$ and $Sb(C_6H_4Cl)O$, which gives $CH_2Ph{\cdot}HgCl$ with HCl–EtOH. H. W.

Mercuration of coumarins. D. Chakravarti (J. Indian Chem. Soc., 1935, **12**, 139—140).—A criticism of Naik *et al.* (A., 1934, 1107). Sen *et al.* (A., 1930, 487) have shown that mercuration of coumarin gives 3 : 5-di(acetoxymercuri)-*o*-coumaric acid, not 6 : 8-bisacetoxymercuricoumarin; 6-nitrocoumarin gives 5-nitro-*o*-coumaric acid (cf. Dey *et al.*, this vol., 211), without removal of NO_2. J. W. B.

Trimethyltriallyltriamine and its mercury derivatives. M. Dominikiewicz (Arch. Chem. Farm., 1935, **2**, 160—164).—Allylamine and CH_2O in Et_2O at 0° yield the *compound* $CH_2<^{NR{\cdot}CH_2}_{CH_2{\cdot}NR}>NR$ (R=allyl), b.p. 138—141° (*picrate*, m.p. 139°), which with $Hg(OAc)_2$ in MeOH affords the *acetoxymercuri*-derivative [$R=CH_2{\cdot}CH(OMe){\cdot}CH_2{\cdot}Hg{\cdot}OAc$], readily hydrolysed by aq. NaOH to the corresponding *hydroxymercuri*-compound. R. T.

Manufacture of benzanthronyl selenium compounds.—See B., 1935, 444.

Tin *m*-tolyl derivatives. K. A. Kotscheschkov and M. M. Nad (J. Gen. Chem. Russ., 1934, **4**, 1434—1439).—RMgBr (R=*m*-C_6H_4Me) and $SnCl_4$ in Et_2O give SnR_4, which with $SnCl_4$ affords R_2SnCl_2 (I), m.p. 39—40°, an EtOH solution of which gives R_2SnO on saturation with NH_3, R_2SnS, m.p. 121·5—122°, with KHS, and RHgCl with $HgCl_2$. (I) and $SnCl_4$ (2 hr. at 100°, then 5 hr. at 160—185°, and 2 hr. at 210—215°) yield $RSnCl_3$, b.p. 150—151°/23 mm., which affords *m-tolylstannic acid*, decomp. 295°, when hydrolysed with aq. KOH. R. T.

Action of different radiations on gelatin. P. Kronenberger (Boll. Soc. ital. Biol. sperim., 1934, **9**, 1336—1339). R. N. C.

Combining weight of collagen. J. Beek, jun. (J. Res. Nat. Bur. Stand., 1935, **14**, 217—225).—The adsorption of aq. HCl (0—1·7*M*) by collagen (I) in presence of saturated or nearly saturated aq. NaCl has been measured. The absorption is reversible. There is a series of < 3 N-containing groups in (I) which react with HCl, forming salts with varying hydrolysis consts. 3N in each unit of 38 are in groups which are much more basic than the remainder. The apparent equiv. of (I) in dil. acid solution is approx. 1000. H. J. E.

Fractionation of gelatin. Different forms of gelatin.—See this vol., 701, 702.

Fractionation of gluten dispersed in sodium salicylate solution. A. G. McCalla and R. C. Rose (Canad. J. Res., 1935, **12**, 346—356).—The pptn. of gluten (I) from solutions of Na salicylate by $MgSO_4$ yields fractions having progressively more amide-N and less arginine-N except for the final 10—15% which is probably a definite protein. The fractions all differ in composition from (I) but when united, dissolved, and repptd. produce the original (I). The customary fractionation into glutenin and gliadin is purely arbitrary, only one protein complex being concerned. A. G. P.

Semi-micro-volumetric determination of organically combined halogen. W. Kimura (Fettchem. Umschau, 1935, **42**, 32—34, 41—46; cf. this vol., 183).—The original Stepanow–Bacon titrimetric method, whilst satisfactory for fatty-aromatic compounds containing halogen in the aliphatic chain, fails for compounds such as *p*-chloro-ω-elaidylacetophenone, where the halogen is in the aromatic nucleus. E. L.

"Nitroguanylhydrazones" of some common aldehydes and ketones. W. F. Whitmore, A. J. Revukas, and G. B. L. Smith (J. Amer. Chem. Soc., 1935, **57**, 706—707).—CO-compounds (1—5 drops or 0·05 g. in 1 ml. of H_2O or pure MeOH), *N*-nitro-*N'*-aminoguanidine (5 ml. of aq. solution saturated at 70°), and AcOH (0·25 ml.) at room temp. or 0° give very rapidly *N-nitroguanylimines* (termed *nitroguanylhydrazones*), $NO_2{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}N{:}CRR'$, which slowly decompose in light and are hydrolysed by hot 20% HCl. They are suitable for identification purposes. *Compounds* from the following are described: *p*-OMe·C_6H_4·CHO, m.p. 200°; PhCHO, m.p. 188°; CHPh:CH·CHO, m.p. 186°; citral, m.p. 135—136·5°; CH_2O, m.p. 169°; piperonal, m.p. 220°; vanillin, m.p. 186—187°; *o*-OH·C_6H_4·CHO, m.p. 213°; $COMe_2$, m.p. 164—165°; COPhMe, m.p. 161—162°; $CH_2Ac{\cdot}CO_2Et$, m.p. 130—131°; *cyclo*hexanone, m.p. 161·5°, explodes at high temp.; COMeEt, m.p. 136·5°; COMePr, m.p. 109—110°; COMeBu, m.p. 109—110°; $AcCO_2H$, m.p. 181·5°. M.p. are corr. R. S. C.

Chloranil, a differentiating reagent for amines. J. Siradjian (Bull. Soc. chim., 1935, [v], **2**, 623—625).—The reaction (B., 1931, 696) whereby chloranil gives red, violet, and emerald-green colorations with, respectively, primary, *sec.*-, and *tert.*-amines affords a general test for these substances. Certain exceptions are noted. J. W. B.

Analysis of pentosans. Condensation reactions furfuraldehyde–phloroglucinol, methylfurfuraldehyde–phloroglucinol, and the separation of furfuraldehyde, methylfurfuraldehyde, and hydroxymethylfurfuraldehyde by means of their phloroglucides. F. Trost (Boll. Soc. adriatica Sci. natur. Trieste, 1932, **31**, 5—30; Chem. Zentr., 1934, ii, 3800).—The composition of the phloroglucides of furfuraldehyde (I) and methylfurfuraldehyde (II) depends on the proportions of reactants employed. If the proportion is 1 : 1, furfuraldehydephloroglucide (III) is $C_{11}H_8O_4$, and methylfurfuraldehydephloroglucide $C_{12}H_{10}O_4$. (I) and (II) are separated from hydroxymethylfurfuraldehyde by rapid steam-distillation, and (I) from (II) by boiling the phloroglucides with 0·05*N*-NaOH for 1 hr., (III) remaining undissolved. H. N. R.

Determination of indoxyl, indigotin, indirubin, and the indoxyl–thymol complex of Jolles. C. O. Guillaumin (Bull. Soc. Chim. biol., 1935, **17**, 403—419).—A comparison is made of the colorimetric methods of determining indoxyl (I) by conversion into indigotin or indirubin and by the (best) method of Jolles (A., 1915, ii, 593), with which, under described conditions, 0·2 mg. of (I) per litre may be detected in 10 c.c. of serum. A. L.

Clinical porphyrin investigations, their quantitative and qualitative technique. R. Fikentscher and K. Franke (Klin. Woch., 1934, **13**, 285—289; Chem. Zentr., 1934, ii, 3801).—Known methods for the determination of porphyrins are discussed; a simple method for small quantities is described. H. N. R.

Morphine reaction with iodic acid in papaverine hydrochloride. J. Rozeboom (Pharm. Weekblad, 1935, **72**, 498—500).—Since $CHCl_3$ dissolves papaverine hydrochloride (insol. in CCl_4 and CS_2) it cannot be used in the KIO_3 test. S. C.

Titration of alkaloid salts and the indicator Poirrier-blue. F. Reimers (Arch. Pharm., 1935, **273**, 140—155).—Alkaloid salts can be titrated with alkali to phenolphthalein in a H_2O–EtOH medium or one which contains $CHCl_3$, or better in a H_2O–EtOH medium with Poirrier-blue (I) as indicator. The absorption curve of (I) in various H_2O–EtOH–HCl and H_2O–EtOH–NaOH mixtures, and the dissociation const. in H_2O and in 50% and 75% EtOH, have been determined. The rate of bleaching of (I) in alkaline solution has been examined. H. G. M.

Biochemistry.

Oxygen dissociation curves of the blood of birds. E. H. Christensen and D. B. Dill (J. Biol. Chem., 1935, **109**, 443—448).—The blood (I) (muscovy duck, domestic fowl, ring-necked pheasant, pigeon, domestic duck, domestic goose) has an affinity for O_2 < that of human blood (II), but the O_2 dissociation curves of (I) and (II) are similar in form. Bird erythrocytes, hæmolysed with H_2O, yield a homogeneous solution (III) of hæmoglobin and a red jelly. The affinity for O_2 of (III) is much < that of whole blood. W. McC.

Determination of oxygen in blood in the presence of ether. J. L. Shaw and V. Downing (J. Biol. Chem., 1935, **109**, 405—417).—A modification of the procedure of Van Slyke *et al.* (A., 1924, ii, 872) is described. The error is < 1%. 1 c.c. of blood is used. W. McC.

Effect of oxygenation and reduction on the equilibrium of hæmocyanin with acids and bases. J. Shack (J. Biol. Chem., 1935, **109**, 383—393).—The $H^{\cdot}$ activity of the serum (I) of the dialysed hæmocyanin (II) of the horseshoe crab (*Limulus polyphemus*) is unchanged by oxygenation (III), but the serum (IV) of the lobster (*Homarus americanus*) is made more acidic by (III), the max. difference in base bound being 0·758 equiv. for each O. (III) decreases the dissociation const. of a diacid or dibasic group by about 0·8—0·9 p_H unit. Titration curves for the oxygenated and reduced forms of (I), (II), and (IV) are given. W. McC.

Absorption spectrum of the carbon monoxide-hæmochromogen. R Hoffmann and W Schwarzacher (Z. physiol. Chem., 1935, **232**, 199—201).—Muscle kept at 60° in presence of CO forms the CO-hæmochromogen. The absorption max. were determined. J. H. B.

Direct determination of carbamino-compounds of carbon dioxide with hæmoglobin. J. K. W. Ferguson and F. J. W. Roughton (J. Physiol., 1934, **83**, 68—86).—HCO_3' and dissolved CO_2 in hæmoglobin (I) solutions equilibrated with CO_2-containing gas mixtures are pptd. by rapid mixing with 6% $BaCl_2$ in NaOH solution and $NaHCO_3$ solution of suitable concn., followed by immediate centrifuging at 1° to remove the $BaCO_3$. The carbamino-compounds (II) of CO_2 and (I) remain in solution, and the CO_2 is determined gasometrically. R. N. C.

Chemical relationships and physiological importance of carbamino-compounds of carbon dioxide with hæmoglobin. J. K. W. Ferguson and F. J. W. Roughton (J. Physiol., 1934, **83**, 87—102).—CO_2 forms carbamino-compounds (I) with hæmoglobin (II) at p_H 7; the amount of combination at a given CO_2 pressure increases with p_H, but is reduced by rise of temp. and oxygenation of (II), these effects being probably due to changes in the no. and character of the uncharged NH_2 groups in the (II) mol. Carbamino-CO_2 amounts to approx. 2% of the total CO_2 in oxyhæmoglobin, and approx. 10% in (II), at 37°, p_H 7·0—7·4, and a CO_2 pressure of 30—60 mm. It is inferred that (I) play an important part in CO_2 transport in the respiratory cycle. Evidence is given suggesting that another form of bound CO_2 ("*y*-bound") is present besides (I) in blood. R. N. C.

Measurement of red-cell volume. V. Behaviour of cells from oxalated and from defibrinated blood in hypotonic plasma and saline. E. Ponder and E. J. Robinson (J. Physiol., 1934, **83**, 34—38).—The red cell behaves as a more "perfect" osmometer in hypotonic defibrinated serum (I) than in oxalated plasma (II), if the tonicity is < 0·6. It behaves as an "imperfect" osmometer in (I) and (II) if the tonicity is < 0·6, and also in hypotonic NaCl solution, losing osmotically-active substances into the surrounding medium if the latter differs considerably from normal. The H_2O content, "critical vol." (III), and "perfection" of the cell as an osmometer, which three factors control the critical tonicity of the cell, behave in accordance with the above view. (III) in serum or plasma is > in NaCl solution. R. N. C.

Determination of fructose in blood. L. D. Scott (Biochem. J., 1935, **29**, 1012—1016).—Fructose is determined in the $ZnSO_4$–NaOH filtrate of blood by addition of Na tauroglycocholate in EtOH (A., 1934, 1019), evaporation to dryness and addition of conc. HCl, and comparison of the purple colour developed with a standard. The fructose content of venous blood is < that of capillary blood. H. D.

Relationship of blood-sugar level to systemic blood-pressure. H. Kosterlitz (Proc. Roy. Soc., 1935, **B**, **117**, 436—454).—When liver-glycogen (I) is min., a fall in blood-pressure (II) below a crit. val. (45 mm. of Hg for the rat) produces a decrease in blood-sugar, which is re-established on restoration of (II). With ample (I), a fall in (II) is accompanied by hyperglycæmia. H. G. R.

Origin of the hyperglycæmia caused by centripetal excitation of the dog's vagus nerve divided at the neck. J. Malméjac and C. Dumazert (Compt. rend. Soc. Biol., 1935, **118**, 1343—1345).—The hyperglycæmia is not due to a depressor effect, and it is not related to the vasodilation. H. G. R.

State of combination of cholesterol in blood-serum. O. Mellander (Biochem. Z., 1935, **277**, 305—313; cf. Theorell, this vol., 188).—Examination of blood-serum by the cataphoretic method shows that partial separation of the albumin (I) from the globulin (II) is thus effected. At least part of the cholesterol (III) exists free or very loosely bound. After cataphoresis zones containing (I) and (III) but no (II), and those containing (II) free from (III) and (I) free from (III) are found, whilst the ratios (III) : (I) and (III) : (II) vary in different part of the tube. If (III) is united to protein at all, then it is to one of the fractions of (I) or (II), and not to them as wholes. W. McC.

Cholesterolæmia after infra-red irradiation of the castrated dog. S. Malczynski and J. Lankosz (Compt. rend. Soc. Biol., 1935, **118**, 1367—

1369).—The cholesterolæmia is independent of the reticulo-endothelial system and of the ovaries. H. G. R.

Determination of free cholesterol by digitonin. R. GOFFINET (Compt. rend. Soc. Biol., 1935, **118**, 1481—1483).—Proteins are pptd. from serum or plasma with $COMe_2$, and the ppt. is extracted for 6 hr. with the filtrate. Cholesterol is pptd. from the solution with digitonin, washed, dried, and weighed. R. N. C.

Physico-chemical studies of fish blood. Neutralisation and buffer-coefficient curves. A. A. DRILHON and G. FLORENCE (Compt. rend. Soc. Biol., 1935, **118**, 1320—1323).—The curves for *Muroena* and fresh- and salt-H_2O eels show a qual. but not a quant. similarity. H. G. R.

Supposed coagulation of oxalate plasma by trypsin. J. MELLANBY (Proc. Roy. Soc., 1935, **B**, **117**, 352—357).—Coagulation of oxalate plasma (I) by trypsin (II) is due to the conversion of prothrombase into thrombase by $Ca^{\cdot\cdot}$ present in (II), the quantity of Ca required depending on the thrombokinase in (I). H. G. R.

Blood-coagulation. I. Rôle of prothrombin and of platelets in the formation of thrombin. II. Formation of fibrin from thrombin and fibrinogen. H. EAGLE (J. Gen. Physiol., 1935, **18**, 531—545, 547—555).—I. Solutions of prothrombin (I) liberate thrombin (II) on the addition of $Ca^{\cdot\cdot}$, whether fibrinogen is present or not. The data indicate that thrombin is a cause, not a product, of coagulation of fibrinogen. Platelets or kephalin accelerate the formation of (II), but the amount formed is dependent only on the concn. of (I). Horse, human, rabbit, or dog platelets accelerate the conversion of (I) derived from any of these species.

II. Ca is necessary for the formation of thrombin (I), but may be pptd. as oxalate without affecting the activity of (I) in converting fibrinogen (II) into fibrin. It is calc. that fibrin cannot be a Ca compound unless (II) has mol. wt. $>10^6$. (I) may coagulate >200 times its own wt. of (II), and its action is probably enzymic. F. A. A.

Hypercoagulability of the blood due to intramuscular injection of sodium citrate. D. DE SOUZA and F. D. M. HOCKING (J. Physiol., 1934, **83**, 49—55).—The alkali reserve and coagulability of the blood are increased by intramuscular injections of Na citrate (I) and $NaHCO_3$, and diminished by NH_4Cl. The increased coagulability from (I) is due partly to the increase in alkaline reserve and partly to (II) absorption into the blood-stream. R. N. C.

Kinetics of hæmolysis in cell–taurocholate–serum systems. E. PONDER and A. S. GORDON (Proc. Roy. Soc., 1935, **B**, **117**, 272—288).—The rate of hæmolysis of cells in contact with Na taurocholate (I) may be increased or decreased on the addition of serum (II), according to the conditions. This may be accounted for by assuming that (I) acts partly as a lysin, partly as a sensitiser for the subsequently added lysin (II). F. A. A.

Stability of antivenoms. E. GRASSET and A. ZOUTENDYK (Compt. rend. Soc. Biol., 1935, **118**, 1403—1406).—Cobra antivenoms (I) and that of *Bitis arietans* (II) are stable over long periods in the cold. They are inactivated by heating above 60°; (I) in broth solution at 60° form toxic substances with the solvent. (II) is not affected by changes of p_H, nor are (I) except at p_H 2, when they become toxic. Addition of lecithin has no effect on (I) or (II). R. N. C.

Co-existence in the blood of an animal in a state of anaphylactic presensitisation of a sensitising and of a preserving substance. F. MAIGNON (Compt. rend. Soc. Biol., 1935, **118**, 1295—1298).—The sensitising substance is adsorbed by the antigen, whilst the preserving substance, which inhibits the anaphylactic effect, is not. H. G. R.

Precipitin reactions and viscosity. M. COPPO (Compt. rend. Soc. Biol., 1935, **118**, 1307—1309).—η of the antigen–antibody mixture (I) rises to a max. at 20—40 min. and then falls to a const. val. The max. increase in η corresponds with a max. speed of flocculation and depends also on the vol. of (I) and temp. H. G. R.

Osmotic relationships in the hen's egg as determined by relative vapour pressures. J. M. JOHLIN (J. Gen. Physiol., 1935, **18**, 481—484).—The osmotic pressure of the yolk is $>$ that of the white (cf. A., 1932, 1153; 1933, 522). F. A. A.

Electrical properties of isolated frog skin. R. J. PUMPHREY (J. Exp. Biol., 1934, **11**, 423—432).—The difference of potential between the inner and outer surfaces of the skin acts as an electrode reversible for $K^{\cdot}$, but not for $Ca^{\cdot\cdot}$ or $Na^{\cdot}$. CH. ABS. (*p*)

Collagen. II. Carbohydrate content. W. GRASSMANN and H. SCHLEICH (Biochem. Z., 1935, **277**, 320—328; cf. A., 1934, 671; Sørensen *et al.*, A., 1933, 731).—Collagen (I) from the dried hides of animals (cattle) contains about 1% of carbohydrate (II), which is an equimol. mixture or compound of glucose and galactose. If (II) is lactose and each mol. of (I) is combined with 1 mol. of (II), the mol. wt. of (I) is about 34,500. W. McC.

Vitreous body. W. S. DUKE-ELDER and H. DAVSON (Biochem. J., 1935, **29**, 1121—1129; cf. this vol., 232).—The possibilities of the vitreous body (I) swelling in glaucoma are studied. A gel at its swelling max. at a given p_H takes up further H_2O on changing the p_H suitably; the changes in the elastic properties of (I) on treatment with solutions of KCNS, K_2SO_4, and dil. HCl are to be interpreted as changes in stability as opposed to reversible changes in hydration, and hence it is deduced that (I) originates *in vivo* as a sol–gel change. The muco-protein in (I) is probably an important factor in its stability. A possible mechanism whereby (I) may increase in vol. is shown. H. D.

Fluorescence spectra of the flavins of some animal organs. H. BIERRY and B. GOUZON (Compt. rend. Soc. Biol., 1935, **119**, 101—103).—The flavins from egg-white, guinea-pig liver, and horse-adrenals show fluorescence spectra in the green and yellow, between 515 and 615 mμ. R. N. C.

Asterubin, a sulphur-containing guanidine compound of living organisms. D. ACKERMANN (Z. physiol. Chem., 1935, **232**, 206—212).—The aq.

extract of *Asterias rubens*, L. (I), and *A. glacialis*, L. (II), yields *asterubin* (III), m.p. 272—273° (decomp.). (III) gives no NH_2-N with HNO_2 and contains 2 NMe groups. $KMnO_4$ oxidation affords guanidine. Hydrolysis with aq. $Ba(OH)_2$ gives $NHMe_2$ and carbamyltaurine. Hence (III) is $NH{:}C(NMe_2)\cdot NH\cdot CH_2\cdot CH_2\cdot SO_3H$. (I) yields in the fraction not pptd. by phosphotungstic acid (IV), glycine and taurine, (II) gives in the (IV) ppt. adenine and *d*-arginine and in the filtrate, glycine, leucine, and tyrosine in addition to (III). J. H. B.

Boric acid reaction and the structure of the nucleic acids. K. Makino (Z. physiol. Chem., 1935, **233**, 186—188; cf. Böesecken, A., 1913, i, 1147).—Deoxyribonucleoside (I) obtained from extract of ox intestine by treatment with nucleotidase reacts positively to the H_3BO_3 test (II). Hence the nucleosides (III) have a pyran ring structure, and consequently the PO_4 of (I) is attached to the 3rd or 4th C of the ribose residue. The mixture obtained by digesting thymonucleic acid (IV) with pancreas-polynucleotidase (free from nucleophosphatase) reacts negatively to (II). Hence deoxyribonucleotides contain no OH corresponding with that of (III) which is phosphorylated. (II) is positive with adenosine, guanosine, inosine, and uridine, and negative with adenylic, guanylic, cytosylic, uracylic, and yeast nucleic acids, and (IV). W. McC.

Determination of reduced glutathione in tissues. A. Fujita and D. Iwatake (Biochem. Z., 1935, **277**, 284—292).—The accuracy of the iodometric determination of reduced glutathione (I) in biological material (II) is increased by deproteinising with HPO_3 (which prevents interference by $Fe^{...}$) and by freezing (II) immediately after the death of the animal from which (II) is taken (prevention of interference by cysteine). Interference by ascorbic acid (III) is avoided by colorimetric determination by the nitroprusside method after removal of protein with HPO_3 and addition of KCN and NH_3 in order to increase persistence of the colour. The (I) and (III) contents of animal organs are given. In addition to (I) and (III), kidney contains other substances which react with I. W. McC.

α–β transformation of muscle-protein *in situ*. W. T. Astbury and S. Dickinson (Nature, 1935, **135**, 765).—The predicted α–β transformation (this vol., 376) on stretching myosin has been accomplished by stretching the sartorius muscle of the frog and the retractor muscle of the foot of *Mytilus edulis*. L. S. T.

Pantothenic acid content of animal tissues. E. Rohrman, G. E. Burget, and R. J. Williams (Proc. Soc. Exp. Biol. Med., 1934, **32**, 473—474).—Pantothenic acid is present in all tissues in measurable amounts. The liver shows the greatest content, but the val. is relatively low in the fresh liver, increasing through autolysis on keeping. R. N. C.

Thyroxine and di-iodotyrosine content of the fœtus and the new-born. A. W. Elmer and M. Scheps (Compt. rend. Soc. Biol., 1935, **118**, 1370—1372).—Thyroids of foetus and the new-born contain 1·3—12·3 and 10·6—11·3 total I, 0·6—3·2 and 5·2—9·8 thyroxine-I, 0·7—9·1 and 5·4—6·0 ($\times 10^{-6}$ g.) di-iodotyrosine-I, respectively. H. G. R.

Distribution of iodine in adrenal cortex and medulla. A. W. Elmer and M. Scheps (Compt. rend. Soc. Biol., 1935, **118**, 1374—1376).—Ox cortex contains 46 and medulla 18×10^{-6} g. per 100 g. of dry gland. The presence of thyroxine could not be demonstrated. H. G. R.

Spontaneous decomposition of lecithin. C. W. Price (Biochem. J., 1935, **29**, 1021—1024).—Following keeping in absence of air, lecithin (I) changes in its electrophoretic behaviour and isoelectric point, the final material more closely resembling (I) *in situ* than that freshly extracted: this is due to removal from the latter of free fatty acids during purification (cf. A., 1933, 778, 1244; this vol., 194). F. O. H.

Fatty substances of shellfish. IV. M. Tsujimoto and H. Koyanagi (J. Soc. Chem. Ind., Japan, 1935, **38**, 118—120B).—The soft bodies of "Kumanokogi" [*Tegula* (*chlorostoma*) *xanthostigma* (A. Adams)], after boiling in H_2O, gave on extraction with Et_2O 0·43% $COMe_2$-insol. phosphatides; 0·56% fat which on saponification yielded acids, m.p. 32·5—33·5°, I val., 153·4, neutralisation val., 196·7, Et_2O-insol. bromides, 40·3%; and cholesterol (20% on fat). The bodies of three "Shako" [*Tridacna gigas* (Linné)] preserved in EtOH gave, on extraction with Et_2O, 0·04% $COMe_2$-insol. matter, 0·9% fat, yielding acids, m.p. 42—43°, I val., 91·3, neutralisation val., 213·5, Et_2O-insol. bromides 16·3%, containing 69·95% Br. The unsaponifiable matter (12·2% on fat) consists of "*shakosterol*" $C_{29}H_{48}O_2$, m.p. 147° (*acetate*, m.p. 156—157°). G. H. C.

Biochemical aspects of fats. I. W. E. Anderson and H. H. Williams (Oil and Soap, 1935, **12**, 65—68).—A discussion of the distribution and function of cholesterol in the organism. G. H. C.

Determination of chlorine in the nervous centres. L. Langeron, M. Paget, and J. Ledieu (Compt. rend. Soc. Biol., 1935, **118**, 1535—1536).—Cl is determined in brain-tissue by the method of Delaville and Broun after drying over H_2SO_4. Cl and H_2O vals. are given for the brains of a no. of patients. R. N. C.

Sodium and chloride in frog muscle. W. O. Fenn, D. M. Cobb, and B. S. Marsh (Amer. J. Physiol., 1934, **110**, 261—272).—The normal Na : Cl ratio (I) in frog plasma is 1·36, and in muscle 2·27. Cl fluctuates > Na in plasma under varying conditions. In muscles soaked in Ringer's solution (I) falls to 1·06 in 5 hr. at 22°; [Na] increases from 24·5% to 33% of the outside concn., whilst [Cl] increases from 14·5% to 31%. In normal muscle *in vivo* 41% of the Na is in excess of the Cl, which diffuses more readily. R. N. C.

Marchi's staining method. III. Artefacts and effects of perfusion. R. L. Swank and H. A. Davenport (Stain Tech., 1935, **10**, 45—52).—The artefacts (I) recognised and investigated in preps. made by Marchi's method are: intrinsic (I), traumatic (I), perfusion (I), and (I) produced by Et_2O anæsthesia. They consist of physically changed myelin. H. W. D.

Poisons of the native toad.—See this vol., 749.

Polypeptides in human saliva. S. DELAUNAY and R. JAHIEL (Compt. rend. Soc. Biol., 1935, **118**, 1418—1420).—Normal human saliva contains polypeptides. R. N. C.

Sodium content of normal cerebrospinal fluid. W. L. DULIÈRE and R. MINNE (Compt. rend. Soc. Biol., 1935, **118**, 1645—1646).—The normal fluid contains 3·35—3·43 g. of Na per litre. R. N. C.

Lipin components of the lymph of the thoracic duct of the dog. S. H. BROCKETT, M. A. SPIERS, and H. E. HIMWICH (Amer. J. Physiol., 1934, **110**, 342—347).—Serum-lipins and the free : total cholesterol ratio are const. in the post-absorptive state. The lipin content of thoracic lymph is ∝ the total fatty acids (I) present. Feeding with fat increases (I), lipin-P, and total cholesterol. The portal vein does not carry (I) from the intestine to the liver during digestion. Injection of adrenaline does not affect (I), but increases glucose and lactic acid in the lymph. R. N. C.

Isolation of 3-hydroxy-6-keto*allo*cholanic acid from pig's bile. E. FERNHOLZ (Z. physiol. Chem., 1935, **232**, 202—205).—Pig's bile after hydrolysis (KOH) gave hyodeoxycholic acid. From the residues after esterification (MeOH–H_2SO_4) and acetylation in C_5H_5N, *Me* 3-*acetoxy*-6-*keto*allo*cholanate*, m.p. 185°, $[\alpha]_D$ −8° in $CHCl_3$, was obtained, indicating the presence of the corresponding acid (*Me* ester, m.p. 135—137°) in the bile. The *allo*-configuration may result from the treatment with KOH. J. H. B.

Intragastric factors in the regulation of gastric acidity. C. M. WILHELMJ, L. C. HENRICH, and F. C. HILL (Amer. J. Physiol., 1934, **110**, 251—260).—The secretion of the whole stomach is composed of an acid secretion (I) and a non-acid secretion (II), [Cl] in the two fractions being 578—604 and approx. 353 mg., respectively, per 100 c.c. (II) is somewhat limited in amount, this being independent of the amount of (I); its alkalinity is 0·04*N*. Total neutral Cl in the isolated stomach is somewhat small, and does not rise as (I) falls. The most important intragastric factor in the regulation of gastric secretion is the intensity of the stimulus for (II). R. N. C.

Isolation of mucoitinsulphuric acid from canine gastric juice. S. A. KOMAROV (J. Biol. Chem., 1935, **109**, 177—187).—The conc. filtered canine gastric juice was hydrolysed at room temp. with NaOH and the product pptd. with EtOH. The ppt. was dissolved in H_2O and poured into AcOH. After washing the ppt. formed with EtOH and Et_2O and drying in vac. the material was extracted with H_2O and again pptd. with AcOH etc. The products were identified as mucoitinsulphuric acid (I), mucoitin, and the Na salt of (I). Mucoprotein (II) (A., 1932, 639) treated as above gave the Ba salt of (I) on treatment with $Ba(OH)_2$. All preps. gave negative biuret and P tests and positive naphthoresorcinol and org. SO_4 tests. The relative yields of (I) prepared from gastric juice directly and from (II) indicated that (I) was present only as an integral part of (II). H. D.

Influence of various anions of the lyotropic series on the sodium and chloride content of fluid in the intestine. H. S. BURNS and M. B. VISSCHER (Amer. J. Physiol., 1934, **110**, 490—498).—H_2O or hypotonic NaCl or urea solutions introduced into the intestine become conc. to vals. > their respective blood concns. (I). Cl accumulation (II) is restrained by Na_2SO_4, NaH_2PO_4, Na citrate, $NaNO_3$, and NaOAc, and disappears from the intestine against a diffusion gradient to reach a concn. < (I); NaSCN, on the contrary, accelerates (II). The effects cannot be explained by simple diffusion or osmosis. R. N. C.

Ante-natal secretion of human mammary gland and comparison between this and that obtained directly after birth. S. T. WIDDOWS, M. F. LOWENFELD, M. BOND, C. SHISKIN, and E. I. TAYLOR (Biochem. J., 1935, **29**, 1145—1166; cf. A., 1930, 805).—Three classes of ante-natal milk (I) differing in their viscosity are obtained independently of the absence or presence of previous lactation or the period of pregnancy. The protein, ash, Cl′, and Ca : P ratio of (I) are > in post-natal milk (II). The Ca, P, and sugar contents of (I) are < in (II); Ca vals., however, showed considerable variations. The sugar content is related to the viscosity of the secretion. H. D.

Presence of an indophenol-oxidase in fresh raw milk. E. J. BIGWOOD and J. THOMAS (Compt. rend. Soc. Biol., 1935, **118**, 1637—1639).—The action of the indophenol-oxidase of fresh milk is inhibited by CH_2O and KCN, and favoured by urethane owing to the inhibitory effect of the latter on the dehydrogenases. R. N. C.

Oxygen consumption by fresh raw milk. E. J. BIGWOOD and J. THOMAS (Compt. rend. Soc. Biol., 1935, **118**, 1639—1642).—Fresh milk contains an oxidase capable of activating mol. O_2, the action being inhibited by 0·01*N*-KCN; the oxidase is hence not one of the known dehydrogenases, the actions of which are not inhibited by this KCN concn. R. N. C.

Deproteinisation of biological liquids. Application to micro-determination of lactose in cows' milk. M. PAGET and Y. DUPONT (Compt. rend. Soc. Biol., 1935, **118**, 1536—1538).—$K_4Fe(CN)_6$ and $Zn(OAc)_2$ solutions form a suitable deproteinising agent. Lactose in milk is determined micrometrically after deproteinisation by the mercuro-iodometric method. R. N. C.

Influence of fat in fodder on the fat content of cows' milk. Z. MOCZARSKI and J. BORMANN (Polish Agric. Forest Ann., 1934, **33**, 201—208).—The fat content of rape cake did not cause diminution of milk yields if fed at rates < 0·1% of the live wt.; milk-fat yields were, however, lowered. CH. ABS. (*p*)

Effect of ingested cod-liver oil, shark-liver oil, and salmon oil on the composition of the blood and milk of lactating cows. C. M. MCCAY and L. A. MAYNARD (J. Biol. Chem., 1935, **109**, 29—37).—Five cows were given cod-liver oil (I), shark-liver oil (II), and salmon oil (III) for periods of 2 weeks with periods between without oil. The

usual lowering of milk-fat after (I) was observed, but (II) and (III) did not appear to have the same effect. The non-saponifiable fraction of (I) has no effect on milk-fat, whilst the triglycerides appear to carry the injurious fraction. No relation was found between oil feeding and composition of blood other than the increase of I val. of plasma-lipins. The total lipins of mammary plasma were consistently lower than those from blood. Neither lipin-P nor inorg. P vals. of the plasma supported the view that phospholipins are the blood precursors of milk-fat. Feeding pasture grass to cows does not counter-effect the lowering of milk-fat after (I). P. W. C.

Uric acid and urochrome in urine. M. Rangier (Bull. Soc. Chim. biol., 1935, **17**, 502—518; cf. A., 1933, 738).—By adsorption on C and elution with aq. NH_3 a solution of the uric acid–urochrome (I) complex present in urine is obtained. From this on treatment with aq. NH_3, uric acid (II) is pptd., the urochrome (III) being obtained after concentrating and adding EtOH. At p_H 6·2, (II) and (III) unite to give (I). A. L.

Urinary lyochromes. W. Koschara (Z. physiol. Chem., 1935, **232**, 101—116).—The purest preps. of uroflavin (I), although agreeing in most properties with lactoflavin, show a C content 1% less. (I) is probably a mixture of lyochromes (II). H_2S decomposes (II) slightly, and should be avoided in later stages of purification. Human urine contains, in addition to (I), aquoflavin, and two other (II), differentiated by chromatogram (III) and behaviour on alkaline photolysis. A method of determination of (II) uses (III) in conjunction with a $KMnO_4$ treatment. Human urine contains in winter $< 10^{-5}$ g., in summer $3—5·5 \times 10^{-5}$ g., of (II) per 100 c.c. J. H. B.

Determination of nitrate–nitrite-nitrogen in urine. R. Gootz and H. Tunger (Z. physiol. Chem., 1935, **233**, 67—74).—0·5 g. of Na_2CO_3 is added to 20—50 c.c. of urine made alkaline with 2*N*-NaOH and the liquid is evaporated to dryness at low temp. ($> 60°$) in a vac. The apparatus is filled with CO_2, 50 c.c. of 80% aq. H_2SO_4 and 3—4 c.c. of Hg are added to the residue, and the whole is vigorously shaken for 15 min. Then a saturated solution of Na_2SO_4 in 80% aq. H_2SO_4 is added and the mixture of gases present is passed over CuO and Cu at low red-heat into a nitrometer. Only N united to O is determined. The error is 16%. W. McC.

Urinary calcium debit and polyuria from ingestion of water. H. Goffart and L. Brull (Compt. rend. Soc. Biol., 1935, **118**, 1630—1632).—Increase of polyuria from ingestion of H_2O is accompanied by a proportional increase of urinary Ca debit, which stabilises itself at a val. $>$ the initial val. R. N. C.

Relationship of the urea clearance to the renal blood-flow. D. D. Van Slyke, C. P. Rhoads, A. Hiller, and A. Alving (Amer. J. Physiol., 1934, **110**, 387—391).—Urea clearance in dogs is $\propto$ renal blood-flow. R. N. C.

Crystalline stercobilin. C. J. Watson (Z. physiol. Chem., 1935, **233**, 39—58; cf. A., 1934, 98, 915).—More detailed chemical and crystallographic examination of the stercobilin (I), its salts (hydrochloride, hydrobromide), and the $FeCl_3$ compound and its ester indicates that the substance of Heilmayer *et al.* (A., 1934, 1386) is identical with (I). Possibly (I) and its salts form loose compounds with $CHCl_3$ and EtOH, which have absorption spectra different from that of (I). The formula for (I) is probably $C_{33}H_{46}O_7N_4$ or $C_{33}H_{46}O_6N_4$. Reduction of (I) does not give mesobilirubinogen (II). A cryst. substance produced by the action of air and light on (II) is not identical with (I). W. McC.

Distribution of sterols in human fæces. Ileal contents. J. A. Gardner, H. Gainsborough, and R. M. Murray (Biochem. J., 1935, **29**, 1139—1144).—Ileostomy and cæcostomy excreta contained only cholesterol and traces of β-cholestanol; hence coprosterol is formed in the colon. H. D.

Diet and disease. S. J. Cowell (Nature, 1935, **135**, 716—718). L. S. T.

Carbon monoxide in the blood in illness. M. Loeper, E. Bioy, J. Tonnet, and A. Varay (Compt. rend. Soc. Biol., 1935, **118**, 1309—1310).—High vals. are observed in asthma, diabetes, and rheumatism. H. G. R.

Spectrography of normal and pathological gastric juice, more particularly in pernicious anæmia. L. Karczag (Compt. rend. Soc. Biol., 1935, **118**, 1417—1418).—The substances responsible for the selective absorption shown by the gastric juice (I) are ultrafilterable, and similar to vitamin-B_1 and -B_2 in physico-chemical behaviour. The selectivity of the spectrum of (I) is increased by ingestion of EtOH. The extinction coeff. is increased in a no. of gastric affections, but diminished in pernicious anæmia. The active substances are present in a large no. of the tissues. R. N. C.

Colloid-osmotic (oncotic) pressure. XXXII. Can the displacement of the colloid-osmotic pressure be responsible for the lowering of water excretion in pernicious anæmia? E. Kylin (Acta med. scand., 1934, **82**, 558—566; Chem. Zentr., 1934, iii, 3975).—Serum-albumin and the colloid-osmotic pressure (I) are $<$ normal in pernicious anæmia. H_2O excretion is considerably reduced, and shows no variations parallel with (I). R. N. C.

Use of grain-fed pigeons in the biological assay of liver preparations. M. R. Gurd (Quart. J. Pharm., 1935, **8**, 39—53).—Modified methods of staining show all pigeon (I) erythrocytes to contain some reticulation. Enumeration of the more densely reticulated cells fails to indicate any response to administration of active liver extracts by grain-fed (I) (cf. A., 1933, 414). F. O. H.

Production of cancer by pure hydrocarbons. III. G. Barry, J. W. Cook, G. A. D. Haslewood, C. L. Hewett, I. Hieger, and E. L. Kennaway (Proc. Roy. Soc., 1935, **B**, **117**, 318—351).—140 compounds, mostly polycyclic aromatic hydrocarbons, have been tested for cancer-producing activity (I). Of 71 compounds not related in structure to 1 : 2-benzanthracene (II), only 6 give positive results, of these only 3 : 4-benzphenanthrene having consider-

able (I). 69 compounds related to (II) have been tested, 25 showing positive results. Most of these are derivatives of (II) having substituents in positions 5 or 6 or both, either alkyl groups or saturated or aromatic rings. Other active compounds are 1 : 2-benzpyrene, 1 : 2 : 7 : 8-dibenzanthracene, and 3 : 4 : 5 : 6-dibenzacridine. Additional rings or substitution in the *meso* positions tend to reduce (I). Methylcholanthrene is the most active compound so far tested. F. A. A.

Lactic gelling of serum not specific for cancer. R. Gillier (Compt. rend. Soc. Biol., 1935, **118**, 1324—1325).—The gelling obtained with lactic acid is not sp. for cancer, being obtained with syphilis, tuberculosis, and leprosy. H. G. R.

Poisoning of glycolytic processes. F. Eichholtz and K. Baumgart (Arch. exp. Path. Pharm., 1935, **178**, 161—166).—The inhibition of glycolysis produced in tumour tissue (I) by substances (II) forming complexes with heavy metals (A., 1929, 594) is demonstrable in the intact animal to an extent comparable with that by $CH_2I{\cdot}CO_2H$ or insulin (III). (II) attack different phases of carbohydrate metabolism (IV), and hence produce varying symptoms of general toxicity. Following treatment with (III), but not with (II), the fall in lactic acid content of (I) is parallel to the increased sensitivity to *X*-irradiation, which, together with the decreased sensitivity due to adrenaline, is not related to the changes in (IV). F. O. H.

Intravenous injection in cancer of the products of the ferric chloride–ascorbic acid reaction. F. Arloing, A. Morel, and A. Josserand (Compt. rend. Soc. Biol., 1935, **118**, 1435—1437).—The violet $FeCl_3$–ascorbic acid compound has a therapeutic effect in cancer. R. N. C.

Cystinuria. II. Metabolism of cystine, cysteine, methionine, and glutathione. E. Brand, G. F. Cahill, and M. M. Harris (J. Biol. Chem., 1935, **109**, 69—83).—In a case of cystinuria (I), cystine (II) and glutathione (III) are almost completely oxidised, the latter giving a small amount of extra (II). Cysteine (IV) and methionine (V) are excreted largely as extra (II), only a small amount being oxidised to inorg. S. Only (III) and no (IV) was found in the urine. (II) can be catabolised without previous reduction and (III) without previous hydrolysis. The behaviour of an NH_2-acid is very different, depending on whether it is catabolised as the free acid or as a peptide. (V) is at any rate in part converted into (IV). The (II) excretion in (I) is caused mainly by dietary (V), but the error of metabolism is concerned with the handling of (IV). (II) is not therefore an essential NH_2-acid. P. W. C.

Iodometric determination of blood-sugar in diabetes. H. Bierry, B. Gouzon, and C. Magnan (Compt. rend. Soc. Biol., 1935, **118**, 1350—1352).—The iodometric and Cu-reduction methods give comparable results. H. G. R.

Dangers and injuries in insulin application. E. Wiechmann (Fortschr. Ther., 1934, **10**, 468—476; Chem. Zentr., 1934, ii, 3974—3975).—The means of avoiding excessive insulin hypoglycæmia are described. R. N. C.

Acetonuria in infectious diseases in relation to glycogen insufficiency of the liver. A. Slatineanu, I. Balteanu, M. Sibi, M. Franke, E. Veit, and P. Filden (Compt. rend. Soc. Biol., 1935, **118**, 1595—1598).—Acetonuria (I) in infectious diseases is associated with blood-sugar and fever, and occurs when the glycogen function of the liver is disturbed by febrile conditions. In the absence of glucose incomplete combustion of proteins gives rise to (I). R. N. C.

Specific chemotherapy of milk-fever by the parenteral administration of calcium borogluconate. H. Dryerre and J. R. Greig (Vet. Rec., 1935, **15**, 456—459).—Ca borogluconate is formed when Ca gluconate (I) is dissolved in aq. H_3BO_3 and the solution evaporated; it differs from both the parent substances in cryst. properties, and does not give the H_3BO_3 flame reaction. It is more sol. in H_2O than (I), the solution showing a lower p_H. It exerts a therapeutic effect in milk-fever. R. N. C.

Iodine content of blood and urine and basal metabolism; their value in the diagnosis of thyroid function. A. W. Elmer and M. Scheps (Acta med. scand., 1934, **82**, 126—136; Chem. Zentr., 1934, ii, 3974).—Blood-I (and in severe cases urinary I) rises simultaneously with basal metabolism in hyperthyroidism and falls similarly in hypothyroidism. R. N. C.

Hypothyroidism induced by complete removal of the normal thyroid gland in chronic heart disease. H. L. Blumgart and D. Davis (Endocrinol., 1934, **18**, 693—700).—Basal metabolism (I) begins to fall one week after thyroidectomy (II), and reaches its min. between the 3rd and 9th weeks. Hypothyroidism does not appear until (I) has remained low for some weeks. Serum-cholesterol increases gradually after (II), and continues to increase after (I) has reached its min. Myxœdema is controlled without raising (I) by daily small doses of thyroid. R. N. C.

Bound water in cardiac muscle in relation to ventricular fibrillation. N. D. Kehar and E. V. McCollum (Amer. J. Physiol., 1934, **110**, 485—487).—Ventricular fibrillation produces increase of free and decrease of bound H_2O. R. N. C.

Oxygen utilisation and lactic acid production in the extremities during rest and exercise in subjects with normal and in those with diseased cardio-vascular systems. S. Weiss and L. B. Ellis (Arch. Int. Med., 1935, **55**, 665—680).—In normal subjects O_2 utilisation of the arm and leg is approx. the same; after exercise (I) it is approx. doubled, and returns to normal within 10 min. Lactic acid also rises after (I) with a mixing effect of the circulation. In cases of heart disease a higher basal heart rate with a greater increase and a slower return to normal were observed. H. G. R.

Chemical composition of hydatic liquid. Lemaire and Ribère (Compt. rend. Soc. Biol., 1935, **118**, 1578—1579).—Mean vals. are given for the

fundamental analysis of hydatic liquid. Creatinine, NH_4 salts, and lecithin are normal constituents, but not necessarily cholesterol or inositol. It contains a proteolytic and a glycolytic enzyme, the former acting at p_H 6·7. R. N. C.

Acute agranulocytosis of kala-azar : negative effect of urea–stibamine and neostibosan on blood of normal rabbits. L. S. Zia and C. E. Forkner (Proc. Soc. Exp. Biol. Med., 1934, **32**, 536—538). R. N. C.

Ketonic substances and hepatectomy in the dog. M. Franke and S. Malczynski (Compt. rend. Soc. Biol., 1935, **118**, 1604—1606).—Blood-$COMe_2$ and -$CH_2Ac{\cdot}CO_2H$ rise slightly 1 hr. after hepatectomy (I), and then fall to zero or very small vals. β-Hydroxybutyric acid increases steadily after (I). R. N. C.

Lactacidæmia after extirpation of the liver. M. Franke and S. Malczynski (Compt. rend. Soc. Biol., 1935, **118**, 1607—1608).—Blood-lactic acid rises steadily in dogs after hepatectomy. R. N. C.

Ether-extractable indirect bilirubin in icteric sera. B. Varela-Fuentes and C. Viana (Compt. rend. Soc. Biol., 1935, **118**, 1518—1520).—A further fraction of indirect bilirubin was extracted by Et_2O from the sera of 10 cases of icterus after exhaustive extraction with $CHCl_3$. R. N. C.

Nature of the ether-extractable indirect bilirubin of icteric sera. B. Varela-Fuentes, M. C. Rubino, and C. Viana (Compt. rend. Soc. Biol., 1935, **118**, 1520—1524).—Et_2O-extractable indirect bilirubin (I) is not adsorbed on serum-globulins (II) when these are pptd., nor is it produced by addition of (II) from normal sera to common icteric sera that do not contain (I). (II) are increased and the albumin–(II) ratio is decreased in sera containing (II). R. N. C.

Phosphovanillic reaction of bile salts in tissue extracts of the icteric dog. E. Chabrol, R. Charonnat, and J. Cottet (Compt. rend. Soc. Biol., 1935, **118**, 1316—1317).—The reaction has been used to show the distribution of bile salts in the tissues of jaundiced dogs. H. G. R.

Changes in the serum during malaria therapy. E. Benhamou and R. Gille (Compt. rend. Soc. Biol., 1935, **118**, 1334—1336).—Henry's reaction depends on a rise in the ratio of flocculable albumin to protective colloids, which is brought about by either a rise in pseudoglobulin or a lowering in serum-albumin × cholesterol. H. G. R.

Rôle of cholesterol in melano-flocculation (Henry reaction). E. Benhamou and R. Gille (Compt. rend. Soc. Biol., 1935, **118**, 1573—1575).—Addition of cholesterol (I) to serum does not increase the intensity of melano-flocculation (II). The increased opacity is due to the additive effects of (II) and pptn. of dissolved (I). Et_2O extraction does not remove any other substance that can increase (II); on the contrary, it increases the index of flocculability. R. N. C.

Relation between pseudoglobulins and "superflocculation" of serum in distilled water. F. Trensz (Compt. rend. Soc. Biol., 1935, **118**, 1332—133).—Qual. differences were observed in the "superflocculation" due to paludism and other pathological states. H. G. R.

Polypeptidorachia in general paralysis. Cyto-polypeptidic dissociation. A. Prunell (Compt. rend. Soc. Biol., 1935, **118**, 1515—1517).—Polypeptides (I) showed increases in the cerebrospinal fluids in cases of general paralysis. R. N. C.

Change of equilibrium in the blood and œdema of the pregnant woman. E. Lévy-Solal and M. Laudat (Compt. rend. Soc. Biol., 1935, **118**, 1325—1328).—Hypoproteinæmia, which occurs early in pregnancy, is not the cause of the œdema which occurs at about 7 months. H. G. R.

Variations of the phosphorus–nitrogen ratio of the bone in the course of experimental rickets in the rat. I. Garcia (Compt. rend. Soc. Biol., 1935, **119**, 109—111).—Bone-H_2O increases with the seriousness of the rachitic lesions. N per g. dry wt. increases, P per g. wet or dry wt. decreases, and the P/N ratio falls below the min. normal val. R. N. C.

Spontaneous calcification of the bone in the course of experimental rickets in the rat : chemical and radiographic tests. I. Garcia (Compt. rend. Soc. Biol., 1935, **119**, 111—114).—Bone-N rises in rickets (I), falling again to normal when calcification (II) begins. P falls in (I) and rises again during (II), but is always < normal. The P/N ratio behaves similarly to P. R. N. C.

Production of methylglyoxal in rachitic tissues. G. Popoviciu and N. Munteanu (Compt. rend. Soc. Biol., 1935, **118**, 1502—1503).—AcCHO increases in the liver and muscles of rachitic animals. R. N. C.

Relation between acetonuria and hepatic insufficiency in scarlatina. A. Slatineanu, I. Balteanu, M. Sibi, E. Butescu, and Z. Paraschivescu (Compt. rend. Soc. Biol., 1935, **118**, 1592—1594).—Acetonuria is as common in patients with hepatic insufficiency as in those without it. R. N. C.

Effect of irradiated ergosterol and calcium lactate on calcification of trichina cysts. W. W. Wantland (Proc. Soc. Exp. Biol. Med., 1934, 32, 438—444).—Irradiated ergosterol and Ca lactate administered to rabbits with trichiniasis cause marked calcification of the cysts, which is not shown by untreated animals. R. N. C.

Significance of Vernes' resorcinol reaction in tuberculosis. V. Chorine and R. Prudhomme (Bull. Acad. Méd., 1934, **111**, [3], 98, 378—382; Chem. Zentr., 1934, ii, 3998).—The resorcinol pptn. depends on a diminution of albumin and a disproportionate increase in eu- and pseudo-globulins, and indicates a disturbance of protein equilibrium. J. S. A.

Uroporphyrin regularly produced in acute porphyrinuria. J. Waldenström, H. Fink, and W. Hoerburger (Z. physiol. Chem., 1935, **233**, 1—9).—The urine of persons suffering from the disease contains a uroporphyrin (m.p. of ester 238—258°) sol. in AcOH and EtOAc. W. McC.

Basal metabolism in old age. J. R. Matson and F. A. Hitchcock (Amer. J. Physiol., 1934, **110**, 329—341).—Basal metabolism in old women is < the standards; results for men agree with the Harris–Benedict standard, but are < the other standards. The metabolic rate is not related to the degree of senility. The sex difference is of approx. the same magnitude as for middle-aged adults. R. N. C.

Respiratory metabolism of infra-human primates. J. M. Bruhn (Amer. J. Physiol., 1934, **110**, 477—484).—Vals. are given for a no. of species of apes and monkeys. The metabolic rate is not altered by extirpation of the frontal cortex. R. N. C.

Chemical aspects of biological oxidations. N. R. Dhar (J. Indian Chem. Soc., 1935, **12**, 96—130).—An address. J. W. B.

Phenosafranine as an anticatalyst of the Pasteur effect. F. Dickens (Nature, 1935, **135**, 762—763).—Phenosafranine (I) is the most vigorous sp. inhibitor of the Pasteur effect yet described. When slices of rat brain are suspended in Ringer's solution containing glucose and (I) in $10^{-5}M$ concn. is added, the carbohydrate respiration of the brain remains unimpaired, the R.Q. remains at the carbohydrate level, but the aërobic acid formation (lactic acid) increases to approx. that found under anaërobic conditions. (I) also inhibits the Pasteur mechanism in tumours. L. S. T.

Biochemical differences between cortex and medullary substance of the kidney. B. Kisch (Biochem. Z., 1935, **277**, 210—222).—As regards the effect on its respiration of hypertonic solutions of salts (NaCl, KCl, $NaNO_3$, Na_2SO_4, K_2SO_4, NH_4Cl), [H·], org. nutrient substances (pyruvate, lactate, glucose), and NH_2-acids (alanine, serine) the cortex (I) of the kidney (II) differs, in some cases greatly, from the medullary substance. Deamination of added alanine occurs only or chiefly in (I). The function of (II) is determined not only by the nature of the blood which passes through it, but also, to an important extent, by that of the urine which it secretes. W. McC.

Mechanism of respiration. K. A. C. Elliot (Nature, 1935, **135**, 762).—Two types of transplantable rat tumour, a sarcoma and a carcinoma, while respiring at a rate equal to that of many other tissues, are unable to oxidise succinic or malic acid. Szent-Györgyi's generalisation that respiration consists mainly of a reversible oxidation of these acids (this vol., 519) is criticised. L. S. T.

Metabolism of tissues excised from adrenalectomised rats. H. E. Himwich, J. F. Fazikas, S. B. Barker, and M. H. Hurlburt (Amer. J. Physiol., 1934, **110**, 348—351).—The respiratory metabolism of the liver, kidney, and diaphragm is unaltered by adrenalectomy; that of the testicle and brain shows a decreased O_2 consumption (I) in absence of glucose, and the R.Q. of the brain is decreased. (I) of the cerebral cortex in presence of glucose is decreased, but this is not due to the inability of the brain to oxidise carbohydrate. R. N. C.

Respiratory quotient of muscle of depancreatised dogs. H. E. Himwich, W. Goldfarb, N. Rakeiten, L. H. Nahum, and D. Dubois (Amer. J. Physiol., 1934, **110**, 352—356).—The R.Q. of the resting leg muscle of the depancreatised dog varies, generally being > 0·7, but occasionally less. Ketones are removed from the blood when the R.Q. is >0·7, but liberated when it is < 0·7, suggesting that the low R.Q. is due to incomplete combustion of fatty acid. R. N. C.

Utilisation of the calorigenic action of di-iodothyronine and thyroxine in muscular exercise. A. Canzanelli, M. Segal, and D. Rapport (Amer. J. Physiol., 1934, **110**, 410—415).—The energy of the calorigenic actions of di-iodothyronine and thyroxine cannot be used for muscular work, and in addition the performance after these substances are given shows a relative "inefficiency" as compared with that under basal conditions, or after meat-protein or tyrosine. R. N. C.

Use of ethyl alcohol as a fuel in muscular exercise. A. Canzanelli, R. Guild, and D. Rapport (Amer. J. Physiol., 1934, **110**, 416—421).—EtOH cannot be used as a source of oxidative energy for muscular exercise. R. N. C.

Pulmonary glycolysis in normal and depancreatised dogs. L. Binet and M. Marquis (Compt. rend. Soc. Biol., 1935, **118**, 1394—1396).—The R.Q. of the air passing through the isolated lung of the normal dog remains steady at unity or oscillates around it, whilst the glucose of the perfusing blood falls. In depancreatised dogs the R.Q. falls after perfusion for 1 hr., whilst glucose increases; the R.Q. can be restored to its initial val. by addition of glucose or insulin to the perfusing blood as required. R. N. C.

Relationship between cell metabolism and growth. E. Bumm (Deut. med. Woch., 1934, **60**, 1173—1176; Chem. Zentr., 1934, ii, 3965).—The significance of glycolysis in the growth, division, and energy supply of the cell is discussed. A. G. P.

Effect of low atmospheric pressure on the glycogen content of the rat. G. Evans (Amer. J. Physiol., 1934, **110**, 273—277).—Total carbohydrate of rats increases considerably when they are starved for 24 hr. at ½ atm.; the greatest increase occurs in the liver, and cannot be accounted for by carbohydrate mobilisation, since no decrease occurs in any of the other carbohydrate stores of the body. It is concluded that the extra glycogen is derived from protein or fat by interconversion. Evidence is given that the process necessitates the presence of adrenal tissue. R. N. C.

Maximum rate of intravenous assimilation of glucose in the resting dog under application of isovolumetric water regulation. M. Wierzuchowski, A. Gostynska, and H. Fiszel (Compt. rend. Soc. Biol., 1935, **118**, 1680—1682).—Continuous intravenous injection of glucose results in glycosuria if the rate of injection (I) is > 1 g. per kg. per hr.; at 9 g. per kg. per hr. 50% of the glucose is excreted. Blood-glucose remains normal until (I) reaches 6 g. per kg. per hr., when it begins to rise rapidly. R. N. C.

Behaviour of lactic acid in blood and urine during continuous intravenous injection of glucose over the whole scale of assimilation. M. Wierzuchowski and T. Chmielewski (Compt. rend. Soc. Biol., 1935, **118**, 1682—1684).—Blood-lactic acid in dogs increases steadily with the rate of continuous injection (I) of glucose. Lactic acid excretion remains low until (I) becomes > 4 g. per kg. per hr., when it increases with (I). R. N. C.

Methylglyoxal and other fission products of anaërobic carbohydrate metabolism. M. Goldenberg, F. Gottdenker, and C. J. Rothberger (Arch. exp. Path. Pharm., 1935, **178**, 201—211).—Intermediate products of anaërobic carbohydrate metabolism other than AcCHO, viz., glyceraldehyde and lactic, pyruvic, glycerophosphoric, phosphoglyceric, hexose-mono- and -di-phosphoric acids, have no action on the heart and blood-vessels. Glyoxal itself is inactive. The rôle of AcCHO in the changes in heart-beat and circulation during exercise and other conditions producing certain types of carbohydrate degradation is discussed. F. O. H.

Heterogonic growth and chemical composition of the liver in pigeons. L. Kaufmann and A. Nowotna (Pflüger's Archiv, 1934, **235**, 247—255).—The liver grows more rapidly than the remainder of the body during the first week of life, H_2O and protein (I) increasing during this time. After the first week growth slackens, and H_2O and (I) decrease. Glycogen (II) rises rapidly during the first 3 weeks, whilst fat falls. (I) increase is isogonic with the liver-wt. (III) during this period, afterwards becoming negatively heterogonic. (II) increase is positively, and fat increase negatively, heterogonic with (III) until the 6th week, after which (II) increase becomes negatively heterogonic and fat increase isogonic. R. N. C.

Ability of various carbohydrates to replace fats in diets containing dried milk. D. J. Levine (Z. Vitaminforsch., 1935, **4**, 92—105).—The subnormal liver-glycogenesis (I) in rats fed on fat-free dried milk is increased by addition to the diet of glucose or sucrose, to a smaller extent by maltose, and still less by lactose. Addition of bread produces (I) > that due to flours (barley > wheat > rice > maize), which, however, are superior to pure sugars, probably owing to their protein and fat content. The glycogen content of the liver is dependent on diet and rate of growth; for a fixed diet it can be calc. from the latter. F. O. H.

Rôle of placenta in fat metabolism of rabbit fœtus. E. M. Boyd (Biochem. J., 1935, **29**, 985—993).—The phospholipin (I), cholesteryl ester (II), neutral fat (III), and free cholesterol (IV) in the placenta (V) and fœtus (VI) of rabbits were determined from the 14th to 32nd day of pregnancy. The concn. of (I) and (IV) in (VI) increases continuously during pregnancy, whilst in (V), (I) passes through a min. and (IV) increases slowly. (II) passes through a max. in (V) and is unchanged in (VI); (III) rises suddenly in (VI) at approx. the 23rd day, and again becomes const. at a high level, and in (V) it decreases slowly throughout the period studied. The opinion that (V) actively transfers lipins as opposed to behaving as a passive membrane is expressed. H. D.

Fate of dehydrocholic and dehydrodeoxycholic acids in the toad.—See this vol., 749.

Nature of the amphibian organisation centre. I. Chemical properties of the evocator. C. H. Waddington, J. Needham, W. W. Nowinski, and R. Lemberg. **II. Induction by synthetic polycyclic hydrocarbons.** C. H. Waddington and D. M. Needham (Proc. Roy. Soc., 1935, **B**, **117** 289—310, 310—317).—I. Details of experiments previously reported (A., 1934, 551, 1029) are given. The evocator substance (I) from newt bodies and mammalian liver extracts is unsaponifiable and is precipitable by digitonin. A similar active substance can be extracted from crude preps. of glycogen (II): this may account for the activity of (II) claimed by some workers.

II. Details are given of the experiments of which the (positive) results have already been reported (A., 1934, 1029). F. A. A.

Transformations of the nucleotides in heart muscle. I. D. Ferdmann and L. Galperin (Biochem. Z., 1935, **277**, 191—202).—The fraction of the extract of the heart muscle (I) of the dog which contains P compounds hydrolysed by *N*-HCl in 30 min. at 100° consists of adenine dinucleotide (II) and at least one other P compound. About 40% of the pentoses (III) of (I) is in the form of (II). Short autolysis (IV) of (I) in H_2O causes increase (not due to decomp. of nucleoproteins), long (IV) decrease, in the (III) content. At p_H 9·4 presence of Mg restricts production of (III) during (IV). The (II) content of (I) decreases during (IV), but if $Mg^{\cdot\cdot}$ is added the degradation of (II) is retarded. W. McC.

Transformations of adenosinetriphosphoric acid in muscle. I. Dephosphorylation during muscular activity. D. Ferdmann, O. Feinschmidt, and M. Dmitrenko (Biochem. Z., 1935, **277**, 203—209; cf. A., 1933, 736; Lohmann, A., 1934, 1020).—In the frog, muscular activity results in the breakdown of the adenosinetriphosphoric acid (I) of muscle (II), $H_4P_2O_7$ being liberated. Resynthesis of (I) occurs as (II) recovers from fatigue. W. McC.

Formation of adenosinetriphosphoric acid and the rôle of phosphagens. P. Ostern, T. Baranowski, and J. Reis (Compt. rend. Soc. Biol., 1935, **118**, 1414—1417).—Autolysed frog-muscle extract (I) slowly hydrolyses phosphoglyceric acid (II); addition of adenylic acid (III) produces slow formation of adenosinetriphosphoric acid (IV), all the P being converted into (IV) or phosphopyruvic acid (V). If creatine has been previously removed from (I) by dialysis, addition of (II) results in partial formation of (V) without liberation of PO_4'''; (III) then causes a rapid formation of (IV), which contains 50% of the P of the (II) added. Hence the dephosphorylation of (II) takes place in two steps, creatine-phosphoric acid not being an obligatory intermediary. R. N. C.

Proteolysis in regenerating tissues. III. Changes in the activity of tissue-protease during

the regeneration of amphibian organs. V. N. Orechovitsch, N. V. Bromley, and N. A. Kusmina (Biochem. Z., 1935, **277**, 186—190; cf. A., 1934, 1252).—In tadpoles, tissue (I) regenerating up to 3 days after amputation of the tail does not differ from ordinary tissue (II) as regards proteolytic activity (III), but from the 3rd until the 11th day (I) has (III) much > that of (II). After the 11th day (III) of (I) decreases, and reaches the normal val. on the 13th day. Tissue from the residual part of the amputated tail behaves like (I) as regards (III). W. McC.

Effect of intermittent and unequal supply of protein on the nutrition of rats. M. Matsuoka (Bull. Inst. Phys. Chem. Res. Japan, 1935, **14**, 15—16).—Groups of animals are fed a protein-free diet, the protein deficiency being supplied at different intervals, but on a single day. The controls (I), which receive protein every day, grow better than the experimental animals (II), although the food consumption of (I) is inferior to that of (II) on a protein-free diet. The total protein intake of (II) is < that of (I). J. D. L.

Metabolism of *l*- and *dl*-methionine in adult and growing dogs maintained on diets of various protein contents. J. A. Stekol (J. Biol. Chem., 1935, **109**, 147—157; cf. A., 1934, 1392).—Dogs were given a diet until the urinary constituents remained const., when methionine was administered, and the urine was analysed until the output or urinary products returned to normal. 63—71% of *l*- (I) and *dl*-methionine (II) fed to adult dogs on a protein-free diet was retained, and the remainder execreted as inorg. SO_4. 74—100% of (II) in growing dogs maintained on Cowgill's diet was retained. 75—81% of (I) and (II) fed to growing dogs on a low-S diet was retained; N-retention occurred on the day of administration. H. D.

Metabolism of norleucine, *iso*leucine, and valine. Synthesis of phenyl derivatives.—See this vol., 746.

Urea formation in the animal body. H. A. Krebs (Ergebn. Enzymforsch., 1934, **3**, 247—264; Chem. Zentr., 1934, ii, 3523).—Theoretical. R. N. C.

Heat production of muscle and nerve. A. V. Hill (Nature, 1935, **135**, 721—724). L. S. T.

Report of physiological chemist, 1932—1933. F. J. Warth (Imp. Inst. Agric. Res. Pusa, Sci. Rept., 1934, 124—133).—Rations containing CaO 0·73, and P_2O_5 0·47% for young heifers were not improved by mineral supplements.

The composition of milk was not significantly affected by increasing the protein level (I) of the ration above normal requirement. High (I) tended slightly to prolong the lactation period.

Conversion of fresh sorghum (II) into hay increased the crude fibre (III) content and decreased that of sol. carbohydrate (IV). The digestibility of (III) and (IV) was lowered. Rice straw provided just sufficient P but insufficient Ca for mature bullocks. (II) hay contained adequate amounts of Ca and P.

Glycuronic acid is present in all urines from Indian cattle and sheep in amounts which vary considerably with the ration, but are not much affected by high SO_4'' feeding.

A negative SO_4'' and S balance in cattle was changed to a positive one by feeding with Na_2SO_4. Ch. Abs. (*p*)

Influence of nutrition on metabolism. III. Effect of potassium on resting and working metabolism. F. Bruman (Deut. Arch. klin. Med., 1934, **176**, 589—611; Chem. Zentr., 1934, ii, 3520—3521).—Administration to man of 5 g. of K daily (as various salts in weakly alkaline solution) resulted in increased Na elimination, increased Ca retention, markedly increased urinary NH_4, and small increases in urea, total N, creatinine, and creatine. The K given was partly retained. Cl′ excretion was unaffected. Basal metabolism was somewhat increased. During work and the subsequent recovery period O_2 consumption was considerably depressed as a result of the increased nutrient effect. A. G. P.

Theory of narcosis. K. H. Meyer and H. Hemmi (Arch. Sci. phys. nat., 1934, **16**, Suppl., 204—207).—The partition coeffs. of a no. of narcotics between the gaseous phase and oleyl alcohol (I) and between H_2O and (I) were compared with their narcotic activity. It is concluded that all the substances examined are active when their concn. in the body-lipins is between 0·03 and 0·05 mol. per litre. H. D.

Effect of narcosis on water and mineral tolerance in fresh-water animals. E. Huf (Pflüger's Archiv, 1934, **235**, 129—140).—Blood-Cl (I) in *Limnæa stagnalis* (II) is increased on immersion in dil. sea-H_2O (III), NaCl being absorbed through the intestine and skin. (I) falls during narcosis (IV) in (II) and in *Potamobius* (V); the fall is more marked in (II), the wt. of which increases through absorption of H_2O, whilst the wt. of (V) is unaltered. The changes in (II) are reversible if (IV) is of short duration; after more prolonged (IV), (I) remains low when the wt. has reached its initial val. In (V), low (I) after (IV) is restored to the normal by immersion in dil. (III). Blood-Na, -Ca, and -Mg in (II) fall with (I), whilst -K increases. R. N. C.

Action of chloroform on the lipin-phosphorus content of guinea-pig liver. E. Büding (Compt. rend. Soc. Biol., 1935, **119**, 51—53).—$CHCl_3$ poisoning produces an increase of total fat and a fall of lipin-P in the liver, both effects being > those produced in yellow fever. R. N. C.

Narcotic potency of some cyclic acetals. P. K. Knoefel (J. Pharm. Exp. Ther., 1935, **53**, 440—444).—The pharmacological action of the cyclic acetals approaches that of paraldehyde as the structure becomes more similar. H. G. R.

Acetanilide poisoning. S. Payne (J. Pharm. Exp. Ther., 1935, **53**, 401—417).—Ingestion of acetanilide causes anæmia, methæmoglobinæmia, and an increase in blood-PhOH, but no cardiac damage. Prolonged administration produces tolerance. H. G. R.

Distribution of phenol between olive oil and serum. A. Heede and S. Stensig (Dansk Tidsskr. Farm., 1935, **9**, 86—94).—The distribution coeff.

between olive oil and serum differs little from that between olive oil and H_2O (1 : 6). R. P. B.

Acetonitrile test for thyroid. F. Wokes (Quart. J. Pharm., 1935, **8**, 54—60).—The susceptibility of mice to MeCN poisoning and the degree of protection (I) afforded by thyroid administration are dependent on temp. Thus at 38° the lethal dose is approx. one fifth of that at room temp., whilst (I) is very slight; at 7—18° (I) occurs, but the flatness of the dose–mortality curve indicates the unsuitability of the method. F. O. H.

Relation between chemical constitution and taste. A. Giacalone [with G. Collesano] (Gazzetta, 1935, **65**, 129—131).—The p_H in 1% solution, solubility, and taste of NH_2Ac and its Cl, Cl_2, Cl_3, Br, Br_2, Br_3, and I derivatives are compared. With increase of negative substituents, sweetness increases. E. W. W.

Refractive index of serum during the action of a depressor substance: acetylcholine. L. Jung and M. Pierre (Compt. rend. Soc. Biol., 1935, **118**, 1451—1453).—The circulatory variations produced by acetylcholine have no effect on the refractive index of the serum. R. N. C.

Depressor substances in extracts of intestine. J. H. Gaddum and H. Schild (J. Physiol., 1934, **83**, 1—14).—The depressor effect of intestinal extracts on atropinised cats is due almost entirely to histamine (I), and there is no evidence of any other acid-stable depressor substance. Substance *P* (II) is present in $CCl_3{\cdot}CO_2H$ extracts of the intestine. The adenosine fraction (alkali-stable depressors) is partly destroyed by autolysis or HNO_2 and is pptd. by $COMe_2$; (II) is stable to these agents and is sol. in $COMe_2$. (I) is destroyed by HNO_2 under conditions where (II) is stable. (II) is carried towards the cathode by an electric current. R. N. C.

Response of the isolated uterus of the guinea-pig to histamine. H. J. Phelps (Biochem. J., 1935, **29**, 1043—1047).—Guinea-pig uterus shows an increased response to histamine (I) in alkaline solutions which might be expected if the activity of (I) is due to the apolar adsorption of non-ionised mols. by cell-surfaces. P. W. C.

Quinine action. W. Warasi (Arch. Schiffs- u. Tropen-Hyg., 1934, **38**, 222—232; Chem. Zentr., 1934, ii, 3524).—Adsorption of quinine (I) by erythrocytes (II) $\propto$ (I) concn. and the amount of (II). The adsorption coeff. is 14·7. CO_2 does not displace (I) from (II). In presence of As, (I) does not cause formation of methæmoglobin. R. N. C.

Distribution of quinine in the endocrine organs. M. T. Régnier (Compt. rend. Soc. Biol., 1935, **118**, 1290—1292).—The quinine, 24 hr. after ingestion, in the organs of a dog was comparable in amount to that found in a human fœtus, the mother having absorbed 1·5 g. 12 hr. before parturition. H. G. R.

Morphine, codeine, and their derivatives. VIII. Monoacetyl- and diacetyl-morphine and their hydrogenated derivatives. N. B. Eddy and H. A. Howes (J. Pharm. Exp. Ther., 1935, **53**, 430—439).—Analgesic (I) and toxic (II) effects of morphine and dihydromorphine are increased by acetylation. Whereas (I) and depressant action are decreased by hydrogenation of both mono- and di-acetylmorphine, (II) is increased. H. G. R.

Effects of sympathetic stimulation and of adrenaline on muscle-glycogen. A. B. Corkill, H. P. Marks, and S. Soskin (J. Physiol., 1934, **83**, 26—33).—Sympathetic stimulation (I) and adrenaline both produce a fall of muscle-glycogen (II). Ergotoxine abolishes the effect of (I) without having any sp. effect on (II). R. N. C.

Pharmacological and bactericidal properties of umbellulone. M. E. Drake and E. T. Stuhr (J. Amer. Pharm. Assoc., 1935, **24**, 196—207).—Umbellulone, a ketone from *Umbellularia californica*, produces methæmoglobin from blood *in vitro* and *in vivo* and hæmolysis in men, guinea-pigs, and horses. It has marked fungicidal and bactericidal actions in concns. $\leqslant$ 2·0 and 0·2%, respectively, whilst the phenol coeff. is 6·25. The min. lethal dose in dogs is 0·178 c.c. per kg. body-wt. F. O. H.

Mechanism of cell-stimulation by substances foreign to the body. G. Orzechowski (Arch. exp. Path. Pharm., 1935, **178**, 229—251).—No action on cell growth by substances such as strophanthin can be detected in cultures (pure or containing leucocytes) of fowl's-heart fibroblasts. Menthol has a typical action on the metabolism of yeasts. The sensitivity of cells in cultures appears to be $>$ that *in vivo*. F. O. H.

Bioassay of digitalis. II. New leg-vein and intramuscular guinea-pig methods. J. H. Defandorf (J. Amer. Pharm. Assoc., 1935, **24**, 276—280). H. D.

Effect of caffeine and theobromine on digitalis toxicity. H. B. Haag and J. D. Woodley (J. Pharm. Exp. Ther., 1935, **53**, 465—473).—In normal doses caffeine or theobromine does not affect the toxicity (I) of ouabain, strophanthin, or digitalis. Larger doses increase (I) of all preps. H. G. R.

Active substance of grass-pollen. I. Activation of an active group of small mol. wt. by colloidal substances. C. E. Benjamins, H. A. E. van Dishoeck, and J. L. M. German (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 308—319).—A pollen extract, after ultrafiltration or proteolytic digestion, gives a diminished but positive skin reaction with hay-fever patients. Activity is enhanced by protective colloids (especially proteins). The active principle is therefore of small mol. wt., but it needs a non-sp. colloidal carrier to exert its full activity. E. A. H. R.

Complexes formed by bromoacetic acid and organic bases and toxins. L. Genevois and G. Mandillon (Compt. rend. Soc. Biol., 1935, **118**, 1353—1354).—Complexes are formed with org. bases, *e.g.*, strychnine, NH_2-acids, and toxins at a definite p_H between 6 and 9. H. G. R.

Effect of some substances on the mechanism of formation of β-hydroxybutyric and oxalic acids. P. H. Fleuret (Compt. rend. Soc. Biol., 1935, **118**, 1569—1572).—Methylene-blue in small, slowly-increasing quantities diminishes urinary β-hydroxy-

butyric acid (I) and increases $H_2C_2O_4$ (II) in dogs on a carbohydrate diet; larger quantities diminish (I) considerably and increase (II) slightly at first, both increasing abruptly later. $(NO_2)_2C_6H_3{\cdot}OH$ lowers (I) and (II) in small quantities, but increases (I) considerably in larger quantities. (I) is increased by oxidation inhibitors (III); (II) is lowered by quinine, but increased by other (III). KNO_3 lowers (I) and (II). R. N. C.

Modifications of the metabolism of the thymus through injection of *cyclo*pentyldinitrophenol in the guinea-pig. M. Chèvremont (Compt. rend. Soc. Biol., 1935, **118**, 1473—1476).—Respiration and aërobic and anaërobic fermentation of the thymus rise to max. vals. 30 min. after injection of *cyclo*pentyldinitrophenol, afterwards falling to normal. R. N. C.

Modifications of the radio-sensitivity of the thymus after injection of *cyclo*pentyldinitrophenol in the guinea-pig. M. Chèvremont (Compt. rend. Soc. Biol., 1935, **118**, 1476—1479).—The metabolic acceleration provoked by *cyclo*pentyldinitrophenol in the thymus increases its radiosensitivity. R. N. C.

Action of germanin on diuresis. E. Zunz and O. Vesselovsky (Compt. rend. Soc. Biol., 1935, **118**, 1620—1622).—Intramuscular injection of germanin (Bayer 205) reduces the diuresis following ingestion of H_2O or NaCl or urea solutions. R. N. C.

Salvarsan and galactose assimilation. O. Satke and K. Thums (Z. klin. Med., 1935, **121**, 748—757; Chem. Zentr., 1934, ii, 3523).—Injection of neosalvarsan in persons with normal galactosuria (I) and normal or increased hyperglycæmic difference (II) produces no abnormal (I), but in cases of increased (I) and (II), (I) falls below the upper normal limit. R. N. C.

Biochemistry of lead in blood. J. Teisinger (Biochem. Z., 1935, **277**, 178—185).—Examination by the method of Heyrovský (A., 1932, 1101) of human blood-serum and erythrocytes (I) to which $Pb^{\cdot\cdot}$ has been added indicates that the $Pb^{\cdot\cdot}$ is adsorbed on the colloidal protein, especially that of (I), the resistance of which in hypotonic solutions is thereby increased. Appreciable combination of the $Pb^{\cdot\cdot}$ with $PO_4^{\cdot\cdot\cdot}$ probably does not occur. W. McC.

Action of simple and complex derivatives of manganese, cobalt, and nickel. F. Hendrych and J. Escobar-Bordoy (Arch. exp. Path. Pharm., 1935, **178**, 167—177).— All the compounds investigated produce paralysis of the central nervous system and heart and diminish the blood-pressure, whilst the simple salts are most, and the tervalent complex derivatives least, toxic on intravenous injection. Co^{II} and Ni^{II} salts accelerate the heart, whilst Mn^{II} and Co^{III} salts are inactive. The simple salts paralyse, and the complex augment, the movements of the isolated rabbit's intestine. Co salts and $MnCl_2$ dilate, whilst complex Mn and all Ni salts contract, blood-vessels (frog). F. O. H.

Catalytic action of iron. III. Oral administration. F. Eichholtz and H. Unrath (Arch. exp. Path. Pharm., 1935, **178**, 154—160; cf. A., 1934, 1031).—Conversion of orally administered Fe^{II} into the catalytically active form in mice is approx. 25% of that of subcutaneously injected Fe^{II}. Fe^{III} citrate and, to a greater extent, ferrum reductum have an activity (I) < that of Fe^{II}, whilst saccharated ferric oxide is inactive. With Fe^{II} salts, (I) is independent of the anion. Max. (I) occurs approx. 8 min. after ingestion and then rapidly diminishes. Ascorbic acid, which stabilises Fe^{II}, neither influences (I) nor reduces Fe^{III} in tissue juices. F. O. H.

Possibility of acute poisoning by iron. Comparison with that by manganese. F. Hendrych and K. Klimesch (Arch. exp. Path. Pharm., 1935, **178**, 178—188).—Excessive administration of certain derivatives of Fe produces liver degeneration (I) in rabbits. Ingestion or subcutaneous injection of large amounts of $FeCl_2$ induces no morphological changes, even though by the latter route death occurs with comparative rapidity. Repeated administration of Na Fe^{III} citrate or $FeCO_3$ and also of Na Mn citrate or $MnCl_2$ produces (I). Impairment of kidney function occurs more frequently with Mn than with Fe salts. F. O. H.

Experimental uranium nephritis: action of insulin on acidosis. L. Brull and E. Hairs (Compt. rend. Soc. Biol., 1935, **118**, 1632—1634).—The acidosis provoked in dogs by $UO_2(NO_3)_2$ is due to org. acid accumulation, and is not reduced by insulin. R. N. C.

Skin sensitivity to dichromate. C. E. Hercus and H. D. Purves (Lancet, 1935, **228**, 985—987).—A definite skin reaction has been obtained in a human being with $3{\cdot}3\times10^{-6}$ g. of $K_2Cr_2O_7$ applied externally and with $3{\cdot}3\times10^{-9}$ g. on intradermal inoculation. Attempts at passive transfer failed. L. S. T.

Hyperglycæmia produced by salts. H. Jentgens (Biochem. Z., 1935, **277**, 273—278).—In fasting rabbits, injection of 5 c.c. of *M*- or 2*M*-NaCl, -NaBr, or -NaI results, within 1 hr., in a 1° rise of body-temp. The NaI and still more the NaBr cause increase in the blood-sugar level, but the NaCl does not affect it. W. McC.

Comparison of the effects of potassium iodide and of di-iodotyrosine on basal metabolism. W. J. Siebert and C. S. Linton (J. Pharm. Exp. Ther., 1935, **53**, 418—429).—Di-iodotyrosine causes the same qual. effects as KI in doses which contain the same amount of I. In thyroidectomised guinea-pigs, the basal metabolic rate is lowered and the rise caused by thyroxine is prevented. H. G. R.

Chemical basis of mud therapy. V. Kilian (Arch. exp. Path. Pharm., 1935, **178**, 197—200).—The application of medicinal mud (Pištany) to the shaved skin of rabbits is followed by an absorption of free and combined S resulting in the presence of H_2S in the blood. Inflammation especially associated with the lymph-glands occurs. F. O. H.

Chronic toxicosis in dairy cows due to ingestion of fluorine. P. H. Phillips, E. B. Hart, and G. Bohstedt (Wisconsin Agric. Exp. Sta. Res. Bull., 1934, No. 123, 30 pp.).—The crit. margin of tolerance of F for dairy cows is 2—3 mg. per kg. body-wt.

Higher proportions caused loss of wt. and reduction in milk yield, lowered food consumption, and inanition. Addition of 1·25—2·50% of raw rock phosphate to the ration caused F cachexia. No influence on the F content or nutritional val. of the milk was detected. Ingestion of F is followed by storage of F in inactive tissues (bones and teeth). More active organs (liver) have very low F contents. A. G. P.

Absorbability of calcium compounds. A. R. Bliss, jun., and R. W. Morrison (J. Amer. Pharm. Assoc., 1935, 24, 280—285; cf. A., 1934, 1133).—The absorption of Ca lactate (I), gluconate, chloride, inositolhexaphosphate, phosphate, and glycerophosphate is measured in mice by its antagonistic action to Mg narcosis. (I) is most rapidly absorbed. H. D.

Injectable calcium salts. A. Lumière and H. Brun (Compt. rend. Soc. Biol., 1935, **118**, 1453—1455).—Org. Ca salts are only very feebly toxic when injected intravenously; when injected subcutaneously or intramuscularly only those of acids derived from sugars are absorbed. R. N. C.

Cardio-stimulatory form of calcium. K. Pohle (Arch. exp. Path. Pharm., 1935, **178**, 109—147).—The Ca of body-fluids occurs as $Ca^{\cdot\cdot}$ and as free or protein-bound complexes (I) (containing PO_4 and fatty acids), an equilibrium existing between $Ca^{\cdot\cdot}$ and (I). PO_4 and high fatty acids which ppt. Ca *in vitro* increase the action of Ca on the heart (II) even with Ca deficiency; hence the action of Ca on (II) depends not on $Ca^{\cdot\cdot}$ but on (I). Strophanthin causes a liberation of Ca by the perfused tortoise's (II), the alteration in the three Ca fractions being due not to ionisation of Ca, but to removal of (I) by adsorption. *Digitalis* preps., however, appear to enter into (I) to an extent modified by disease of (II). F. O. H.

Analysis of fatigue in nerve–muscle preparations. I. Walidow (Pflüger's Archiv, 1934, **235**, 147—155).—Perfusion of a previously fatigued nerve–muscle prep. with Ringer's solution containing 0·06—0·2% Ca produces augmentation of the muscular spasms. The effect is due to the action of Ca on the nerve-endings, the "local fatigue" of which is abolished. Ba has a feeble effect, whilst Mg and Sr are without effect. R. N. C.

Effect of γ-irradiation on growth and nitrogenous metabolism of the protozoon *Bodo caudatus*. N. R. Lawrie and M. Robertson (Biochem. J., 1935, **29**, 1017—1020).—γ-Irradiation from Ra produces first a decrease in NH_3 production (I) (this vol., 535) coinciding with only a slight response in size and rate of division (II) of the cells; this is followed by a depression of (II) and an increase in (I) and size of cells. The final stage (approx. 20 hr. from start) is characterised by a moderate stimulation of (I), maintenance of increased size, and absence of any marked effect on (II). F. O. H.

Photolethal effects of quartz ultra-violet radiation on *Paramecium*. A. C. Giese and P. A. Leighton (J. Gen. Physiol., 1935, **18**, 557—571).—The absorption by *Paramecia* of radiation of wave-lengths 2804, 2654, and 2537 Å. is about equal; it is less for wave-lengths 3025 and 3130 Å. All these except 3130 are photolethal, from 8 to 10×10^{12} quanta per *Paramecium* being necessary to produce 50% vesiculation. F. A. A.

Determination of the concentration of enzyme preparations. W. R. Johnston and S. Josza (J. Amer. Chem. Soc., 1935, **57**, 701—706).—Enzyme reactions are not strictly unimol. K thus does not accurately define the concn. of enzyme (I). This is best determined by the initial rate of reaction, to which it is often strictly proportional. A "liquefon" is defined as the amount of starch-liquefying (I) which will convert standard starch paste (II) at the rate of 25 mg. of dry starch per min. at zero time under the following conditions: 100 g. of (II), 10 c.c. of infusion containing 0·75—7 mg. of α-amylase (III), diluted to 10 litres, at 21°, viscosities being measured in a modified pipette at intervals during the first 10—20 min. (III) is activated by NaCl, 25 g. per litre giving the max. effect. R. S. C.

Diffusion of the dehydrogenase of higher fatty acids in different organs. F. P. Mazza and G. Stolfi (Boll. Soc. ital. Biol. sperim., 1933, 8, 1780—1781; Chem. Zentr., 1934, ii, 3966—3967).—The oxidising action occurs in liver and in fatty tissues examined by Quagliariello (A., 1933, 747), but not in fresh milk, pancreas, duodenal mucosa, muscle, or kidney extracts. A. G. P.

Tissue metabolism. VI. Lactic dehydrogenase, xanthine-oxidase, and nucleosidase in tumour and muscle extracts. E. Boyland and M. E. Boyland (Biochem. J., 1935, **29**, 1097—1101).—Lactic dehydrogenase (I) similar to that in heart-muscle is present in rat, mouse, and rabbit muscle, and in mouse and rat tumours. Rat and mouse muscle extracts contain xanthine-oxidase (II) and adenine-nucleosidase. Rat and mouse tumour extracts contain (II) and rapidly attack adenylpyrophosphate or (I) co-enzyme. J. N. A.

Components of dehydrase systems. V. Actions of cozymase, Warburg's co-enzyme, and adenylpyrophosphate. H. von Euler, E. Adler, F. Schlenk, and G. Günther (Z. physiol. Chem., 1935, **233**, 120—147; cf. A., 1934, 1257).—Cozymase (I), which is probably not a mixture, acts as co-enzyme in the hexose monophosphate (II) and EtOH-dehydrase (III) (from yeast) systems. (I) and the respiratory co-enzyme (IV) (Warburg) from horse blood-cells are interchangeable in (II), but (IV) cannot replace (I) in (III). (I) and (IV) are interchangeable in the glucose-dehydrase system from liver and probably also in the (III) system from liver. Adenylpyrophosphoric acid shows no co-enzyme action in (II) and (III) and cannot replace (I) in alcoholic fermentation. In (II) purest (I) has about a seventieth of the effect of (IV). (IV) is much more thermolabile than is (I). W. McC.

Cozymase. IV. K. Myrbäck and B. Örtenblad. **V.** K. Myrbäck. **VI. Preparation and properties of highly active cozymase.** K. Myrbäck and B. Örtenblad. **VII. Cozymase from animal organs.** K. Myrbäck (Z. physiol. Chem., 1935, **233**, 87—94, 95—119, 148—153, 154—158;

cf. A., 1934, 1035).—IV. The purification of cozymase (I) (from yeast) is simplified if impurities (II) are removed by pptn. with $Pb(OAc)_2$ instead of with Hg salts, but the yield (50%) is lowered. Subsequent treatment with picric acid may usually be omitted. Partly purified (I) is further purified by removing (II) with benzidine or by pptg. (I) with $UO_2(OAc)_2$. A cryst. *strychnine* (III) salt is obtained which contains about 7 mols. of (III) for each P. After heating with dil. alkali (I) behaves as a dibasic acid. This fact and the N and P contents indicate that (I) is a mononucleotide in which one of the usually free OH groups of the H_3PO_4 residue is substituted with a radical of unknown composition.

V. Active (I) has a strong reducing power which is greatly diminished (to 40% of original val.) by heating at 100° in alkaline solution with proportionate decrease in the activity.

VI. Increased purity is achieved in the isolation of (I) by successive fractional pptn. of (I) with salts of heavy metals and removal of (II) by similar pptn. The purest samples contain 6·7% of P and 14·3% of N (10% of purine-N).

VII. (I) from the organs of the rabbit and dog is identical with that from yeast. W. McC.

Schardinger's milk enzyme. L. Reichel (Naturwiss., 1935, **23**, 260—261).—Milk-aldehydrase dismutes under aërobic and anaërobic conditions and contains no lactoflavin which is responsible for the dehydrogenation observed by Wieland (cf. A., 1930, 248; 1931, 389). J. L. D.

Action of the aldehyde-dehydrogenase of milk on cytochrome-*C*, isolated from yeast. E. J. Bigwood, J. Thomas, and D. Wolfers (Compt. rend. Soc. Biol., 1935, **118**, 1488—1490).—Cytochrome (I) is reduced by aldehyde-dehydrogenase (milk) in anaërobic conditions. In aërobic conditions the reduction is scarcely observed, since the reduced (I) is immediately reoxidised by an oxidase, the action of which is inhibited by KCN. R. N. C.

Enzyme action in relation to the biological effects of radiation. G. Harker (J. Cancer Res. Comm. Sydney, 1935, **6**, 159—161).—The irradiation of indophenol-oxidase by a radon seed has but little effect on its activity, so that if the biological effects radiation on cancer cells are due to modifications of the enzyme reactions, the dehydrogenases are probably affected. E. A. H. R.

Purification of the enzymes which oxidise certain amino-acids. F. Bernheim and M. L. C. Bernheim (J. Biol. Chem., 1935, **109**, 131—140).—Celite is added to a suspension of macerated kidney (I) at p_H 6·9 and, after centrifuging, the celite is extracted with HPO_4'' buffer and Na_2CO_3, and the extract is dialysed. *dl*-Phenylalanine, -alanine, -proline, -leucine, -*iso*leucine, -valine, and *d*-phenylalanine are rapidly deaminated and oxidised by the extract, whereas the natural isomerides are attacked slowly or not at all. The oxidation of the *dl*-mixtures corresponds with the unnatural isomeride. Only proline is oxidised by a liver extract prepared similarly, whereas a suspension of liver cells (II) oxidises all slowly. The oxidations are not inhibited by KCN or F′; methylene-blue is reduced by all the NH_2-acids studied in the presence of the extract, but the rates are not ∝ the rates of oxidation. (I) oxidises *dl*-phenylglycine, whilst (II) does not; glycine is not oxidised by either (I) or (II). H. D.

Destruction of histamine by the lung. L. Binet and M. Marquis (Compt. rend. Soc. Biol., 1935, **118**, 1285—1286).—Lung tissue shows a histaminolytic effect. H. G. R.

Emulsin. XIX. Action of ozone on almond-emulsin. B. Helferich and S. R. Petersen (Z. physiol. Chem., 1935, **233**, 75—80; cf. this vol., 250, 401).—In the ozonisation of org. compounds (I) the amount of O_3 consumed and hence the amount of (I) attacked is determined by adding bromide–bromate solution, conc. HCl, and KI to the solution containing unconsumed O_3 and titrating with $Na_2S_2O_3$. The amount (about 0·0031 g.) of O_3 required to destroy one unit of emulsin (II) is determined. The resistance of (II) to attack by O_3 is unaffected by addition of tyrosine, cystine, or maleic acid, but is slightly increased by that of histidine, phenylalanine, cysteine, $CH_2{:}CH{\cdot}CH_2{\cdot}OH$, or α-glucosidase (III) from yeast (which consume the O_3), and considerably increased by that of tryptophan (IV), glycyltryptophan, or β-indolylacetic acid (which consume part of the O_3). Destruction of (IV) by O_3 is greatest at p_H 5·0—5·7, 1·5 mols. (3 mols. in absence of buffer) of O_3 being required. As regards attack by O_3, β-*d*-galactosidase resembles (II), malt diastase is more sensitive, but otherwise resembles (II), and (III) requires much more O_3 for destruction because it contains a substance which consumes or catalytically decomposes O_3. W. McC.

Salivary, pancreatic, and "*Aspergillus*" amylase as mixtures of two enzymes. G. Giesberger (Proc. K. Akad. Wetensch. Amsterdam, 1935, **38**, 344—345).—The evidence (A., 1934, 1136) afforded by diffusion experiments in gelatin for the dual nature of certain amylases (I) is unsound. On dilution, α-malt (I) gives the same concentric rings as a mixture of α- and β-(I). E. A. H. R.

Preparation of starch substrates for amylase determinations. W. R. Thompson (J. Biol. Chem., 1935, **109**, 201—202).—The method of determination of amylase activity described previously (this vol., 402) is modified by storage of the solution of sol. starch in 0·3*M*-NaOAc at 25° followed by heating to 100° before proceeding. H. D.

Enzymic hydrolysis of sucrose in the presence of formaldehyde. A. Chaudun (Bull. Soc. Chim. biol., 1935, **17**, 519—522).—The influence of CH_2O on the hydrolysis of sucrose (I) by invertase is like that of glycerol, EtOH, and MeOH, viz., the rate of hydrolysis is lowered and at the same time the wt. of (I) in solution when the hydrolysis ceases to be a linear function of time is greater. A. L.

Lactase activity of intestinal mucosa of dog and some characteristics of intestinal lactase. F. A. Cajori (J. Biol. Chem., 1935, **109**, 159—168; cf. A., 1934, 808).—Lactase (I) activity is uninfluenced by phosphates. The Michaelis const. of (I) is 0·006.

(I) is adsorbed readily, from slightly acid solution, by $Al(OH)_3$ or $Fe(OH)_3$. H. D.

Glyoxalase. III. Glyoxalase as a reagent for the micro-determination of glutathione. G. E. Woodward. **IV. Antiglyoxalase action of kidney and pancreas preparations.** G. E. Woodward, M. P. Munro, and E. F. Schroeder (J. Biol. Chem., 1935, **109**, 1—10, 11—27).—III. A manometric method is described for determination of reduced glutathione (I) which depends on the measurement of the activating effect of (I) on $COMc_2$–yeast glyoxalase, the effect being sp. and cysteine, thioneine, ascorbic acid, or oxidised (I) does not produce any activity. (I) vals. for tissues are, but for blood are not, lower than by the iodometric method.

IV. Kidney tissue of rat, rabbit, pig, and horse contains a powerful inhibitor of glyoxalase, which increases with time. The inhibitor destroys the coenzyme (I) without destroying its SH group. The antiglyoxalase effect of pancreas is due to 2 factors, one of which acts on the enzyme, the other resembling the kidney inhibitor. P. W. C.

[Esterase models.] W. Langenbeck (Ber., 1935, **68**, [*B*], 776—777; cf. A., 1934, 509, 849).—On account of the widely differing experimental conditions, the criticisms of Olivier (this vol., 659) are regarded as unjustified. H. W.

Phosphatases. I. Kidney-phosphatase. II. Preparation of highly active phosphatase from animal material. H. Albers and E. Albers (Z. physiol. Chem., 1935, **232**, 165—188, 189—195).—I. A mixture of PhMe and EtOAc is the best autolysing agent for the prep. of phosphatase (I) from animal organs. (I) is purified by fractional pptn. with EtOH. The total (I) content of the fractions is > that of the original solution owing to elimination of inhibitors. The purest preps. (150 units per mg.) still contain Mg salts and inorg. PO_4'''. The product contains no (I) with p_H optimum in the acid range. The mol. wt. of (I) by "free diffusion" is 6000—10,000. Dialysis produces rapid inactivation of (I).

II. The liberation of (I) by PhMe and EtOAc is conducted in presence of EtOH (25—30% actual concn.). This protects the (I) and prevents the dissolution of protein substances. The (I) is then pptd. by increasing the EtOH concn. to 65%. A prep. with an activity of 40—50 units per mg. is thus obtained. J. H. B.

Fermentation enzymes. II. Yeast-phosphatese. A. Schäffner, E. Bauer, and H. Berl (Z. physiol. Chem., 1935, **232**, 213—228).—A redoxase extract of orange-pips can replace the redoxase of yeast in the phosphorylating system containing cozymase (I), hexosediphosphoric acid (II), and MeCHO (III). The intermediate enzyme (IV) of Warburg and Christian can be freed from phosphorylating action by $Al(OH)_3$ C_γ, and is then active only in presence of "yeast-phosphatase" (V), (II), and (III). (V) loses its activity as a component of the system after treatment with $Al(OH)_3$ C_γ; it is now free from zymohexase (VI) and can be replaced by muscle-(VI). (V)-free (VI) and (V)-free (IV) can produce synthesis of hexose ester. (VI) can be omitted if dihydroxyacetonephosphoric acid (VII) replaces (II); thus in the system (VII), (III), (I), hexose, and H_3PO_4, (III) alone is needed. J. H. B.

Degradation of nucleic acid with nuclease from ox-kidney. K. Makino (Z. physiol. Chem., 1935, **232**, 196—198).—From the products of fission were isolated guanylic acid, guanosine, uridine, guanine, hypoxanthine, and xanthine, but no adenosine, cytidine, adenine, cytosine, or uracyl, indicating that the 6-NH_2 is more readily deaminated than the 2-NH_2 in the purine nucleus. J. H. B.

Enzymic histochemistry. XV. Micro-determination of arginase. K. Linderstrøm-Lang, L. Weil, and H. Holter (Z. physiol. Chem., 1935, **233**, 174—180).—Improvements in a modification of the urease (I) method (cf. A., 1933, 1218) are described. Determinations are more rapidly and easily made by titrating liberated ornithine (II) in EtOH+$COMe_2$ (1 : 1) with 0·05*N*-NMe_4·OH in 90% EtOH (indicator: thymol-blue). CO_2 must be excluded. The second method, which determines about 95% of (II), is inapplicable if large amounts of (I) are present. W. McC.

Enzymic hydrolysis of raw and heat-treated egg-white. E. W. Cohn and A. White (J. Biol. Chem., 1935, **109**, 169—175).—The enzymic hydrolysis of egg-white (I) before and after heating is determined by formol titration. Trypsin has little effect on unheated (I) solutions unless previously treated with pepsin. The tryptic hydrolysis increases with the time of pre-heating at 100° of (I) up to 30 min. both with and without pre-treatment with pepsin. H. D.

Action of dyes and narcotics on proteolytic enzymes. Trypsin and papain. K. Basu and R. Chakravarti (J. Indian Chem. Soc., 1935, **12**, 82—88).—Inhibition (≯ 36%) of the hydrolysis of peptone by trypsin (activated by cystine) at p_H 8·67, and by papain (activated by cysteine) at p_H 5·0, at 37° is effected by addition of 0·02% of acid dyes and by some basic dyes, the action being sp. The enzymes must therefore be amphoteric in character. Of various narcotics and other substances investigated only gallic acid, vanillin, and ethylurethane exhibit appreciable inhibiting action, which in all cases increases with time. J. W. B.

Detection of enzymes of the trypsin and papain types. J. B. Sumner and S. F. Howell (J. Biol. Chem., 1935, **109**, 429—431).—The enzymes (I) [trypsin, fig-tree protease, taka-diastase, papain-cysteine, bromelin-cysteine, (I) of extract of green malt, invertase] are detected by allowing them to act, in buffered solution, on hide powder containing pptd. $BaSO_4$ which is liberated, causing turbidity. W. McC.

Influence of oxidising and reducing agents on the activity of papain. III. T. Bersin and H. Köster (Z. physiol. Chem., 1935, **233**, 59—66; cf. A., 1934, 450).—At p_H 5 and 40° papain (I), after oxidation with H_2O_2, is reactivated by the hydrochloride of 3-amino-4-hydroxy-, *p*-acetamido-, or the hydrochloride of *p*-amino-phenylarsine oxide, but is inactivated by *p*-acetamidophenylarsinic acid or its Na H salt. Reversibly oxidised (I) does not

coagulate milk. The action of (I) is explained by supposing that its NH_2 group, activated by dipole induction, reacts with a CO·NH (probably terminal) in the substrate, (I) being subsequently regenerated by hydrolysis. W. McC.

Crystalline chymotrypsin and chymotrypsinogen. I. Isolation, crystallisation, and properties of a new proteolytic enzyme and its precursor. M. Kunitz and J. H. Northrop (J. Gen. Physiol., 1935, **18**, 433—458; cf. A., 1934, 219).—The activation of cryst. chymotrypsinogen (I) by trypsin (II) follows a unimol. course and the rate is a max. at p_H 7—8. The product, chymotrypsin (III), has the same mol. wt. as (I), but 6 more primary NH_2-groups. (III) clots milk but not blood-plasma, and hydrolyses sturine, caseinogen, gelatin, and hæmoglobin more slowly than does (II). (III) attacks caseinogen at different linkings from those attacked by (II), and does not attack di- or poly-peptides. (III) may be inactivated by pepsin digestion, heat, or acid. F. A. A.

Determination of the rennet activity of chymotrypsin. M. Kunitz (J. Gen. Physiol., 1935, **18**, 459—466).—Milk powder solution+chymotrypsin flow through a graduated tube at a determined rate. The graduation reached when the milk clots gives the time taken. F. A. A.

Monolayers of proteolytic enzymes and proteins. III. Enzyme reactions and penetration of protein monolayers. J. H. Schulman and A. H. Hughes (Biochem. J., 1935, **29**, 1236—1242).—A fatty acid–protein complex which can be extracted from pancreatin (I), but not from the sp. proteolytic enzymes, simulates the action of (I) on monolayers (II) of proteins and fats, and accounts for the reported activity of bulk-inactive preps. of (I) on such (II). The action of chymotrypsin, chymotrypsinogen, and cryst. pepsin on (II) of protein and tripalmitin is described. F. A. A.

Effect of halogen salts on the clotting of milk by trypsin. W. M. Clifford (Biochem. J., 1935, **29**, 1059—1063).—Milk gives a firm clot with trypsin if the halogen salts of Li, Na, K, NH_4, Mg, Ca, or Ba are added, the coagulating action being least with the fluorides and the alkaline-earth metals being only slightly more efficient than the alkali metals. Mg salts are less powerful than those of Ca or Ba. At concns. above 0·25*M* the salts of Mg, Ca, Ba are less effective than at concns. between 0·125 and 0·015*M*. P. W. C.

Activation of cathepsin. E. Waldschmidt-Leitz and K. Bartunek (Z. physiol. Chem., 1935, **233**, 36—38).—Since most of the activator (I) (*e.g.*, in spleen) seems to be bound in the form of a symplex to insol. cell-substance of high mol. wt. and requires to be liberated and made sol. by treatment with glycerol, results derived from investigation of pulped or minced tissues or extracts of them are untrustworthy. Living material should be used. W. McC.

Physico-chemical factors in the interferometric technique of Hirsch. A. Grigaut and E. Bettend (Bull. Soc. Chim. biol., 1935, **17**, 420—431).—The fall (I) in the concn. of sera often shown in the application of the interferometric method of Hirsch indicates that, apart from enzymic and H_2O-absorptive actions which take place, there are in addition phenomena of adsorption which cause (I) and depend on the physical nature of the different sera. A. L.

***Saccharomycetes* and other fungi still alive in the pure cultures of Hansen and Klöcken.** O. Winge and A. Hjort (Compt. rend. Trav. Lab. Carlsberg, 1935, **21**, 51—58).—Several cultures kept in 10% sucrose or beer wort since 1886—1922 are still living. E. A. H. R.

Mechanism of fermentation of dihydroxyacetone. H. Lehmann (Biochem. Z., 1935, **277**, 261—267; cf. Iwasaki, A., 1929, 354).—Dihydroxyacetone (I) on fermentation with *Saccharomyces Ludwigii* is converted into hexosediphosphoric acid (II). (I)-phosphoric acid is a secondary product derived from (II). W. McC.

Effect of dyes on yeast fermentation as influenced by hydrogen-ion concentration. E. Adams and W. J. Robbins (J. Agric. Res., 1934, **49**, 1025—1031).—The toxicity to yeast of rose-Bengal and eosin was greater in the more acid solutions, notably in those having $p_H < 6·0$ and $< 5·0$, respectively. Safranine was more toxic in the less acid solutions, especially at $p_H > 6·0$. Toxicity of brilliant-green increased with falling p_H to approx. 5·5, when pptn. occurred. Dahlia was least toxic in acid solutions, but the influence of reaction was not great. A. G. P.

Action of 2 : 4-dinitrophenol on American baker's yeast (Fleischmann yeast). L. Genevois and P. Créac'h (Compt. rend. Soc. Biol., 1935, **118**, 1357—1359; cf. A., 1934, 1262).—Respiration of Fleischmann's yeast is not increased by 2 : 4-dinitrophenol, but the latter is reduced. H. G. R.

Action of 2 : 4-dinitrophenol on French baker's yeast (Springer's yeast). L. Genevois and R. Saric (Compt. rend. Soc. Biol., 1935, **118**, 1354—1356).—Previous conclusions (this vol., 253) are maintained, contrary to Plantefol (this vol., 405). H. G. R.

Action of 2 : 4-dinitrophenol on yeast respiration. L. Plantefol (Compt. rend. Soc. Biol., 1935, **118**, 1359—1360).—Polemical (cf. preceding abstract). H. G. R.

Action of Röntgen rays on yeast fermentation. V. Gronchi (Strahlenther., 1934, **51**, 319—338; Chem. Zentr., 1934, ii, 3971).—Production of CO_2 from glucose by yeast is stimulated by radiations of 0·37 and 0·16 Å. The effect for hard is > for soft rays. A. G. P.

Nutrition of *Polytoma caudatum*, var. *astigmata* (colourless Chlamydomonadine), and synthesis of starch by leucophytes. A. Lwoff and L. Provasoli (Compt. rend. Soc. Biol., 1935, **119**, 90—93).—Growth of *Polytoma caudatum astigmata* (I) is poor in media lacking AcOH, addition of which accelerates development. AcOH can be replaced by $EtCO_2H$, $Pr^{\alpha}CO_2H$, $AcCO_2H$, or starch, but not by $Pr^{\beta}CO_2H$, *n*-valeric, hexoic, or lactic acid. (I) does not grow rapidly with asparagine or other single NH_2-acid as the sole N source, even in presence of

NaOAc. (I) can synthesise starch through the action of a superficial reticulated leucoplast, similar to those found in chlorophyll-containing organisms. R. N. C.

Variability of monosporic cultures of *Coccomyces hiemalis*. R. O. Magie (Phytopath., 1935, **25**, 26—27).—Variations in colour, growth, acid production, and spore formation were unrelated to the nature of N or C sources utilised. Growth was influenced by temp. and p_H. A. G. P.

Formation of organo-metalloidal compounds by micro-organisms.—See this vol., 738.

Beneficial fungi. C. M. Haenseler (New Jersey Agric., 1934, **16**, No. 2, 6).—*Rhizoctonia* (I) failed to grow in media previously carrying *Trichoderma* (II). Toxin produced by (II) was destroyed by heating to 80° for 10 min., by ageing for 10 days, or by exposure to O_2 for 5 min. Media so treated permitted growth of (I). Ch. Abs. (*p*)

Effect of temperature, salt, and acidity on the growth of *Oospora lactis*. H. Macy and A. E. Anderson (Nat. Butter and Cheese J., 1934, **25**, No. 22, 28—29).—Growth of the mould on whey–agar was affected by 1% and arrested by 10% salt. On buttermilk the corresponding vals. were 2·5 and 10%. Acidity had little influence on growth. Growth was retarded at 10° and 2° and ceased at −23°. Combined effects of high salt concn., low temp., and/or [H·] were observed. Ch. Abs. (*p*)

Biochemistry of micro-organisms. XLIV. Fulvic acid, a new crystalline yellow pigment, a metabolic product of *Penicillium griseofulvum*, Dierckx, *P. flexuosum*, Dale, and *P. brefeldianum*, Dodge. A. E. Oxford, H. Raistrick, and P. Simonart (Biochem. J., 1935, **29**, 1102—1115).—*P. griseofulvum* (I), *P. flexuosum* (II), and *P. brefeldianum* (III), when grown on a synthetic medium containing glucose, NH_4 tartrate, and mineral salts, give rise to a yellow pigment, *fulvic acid*, $C_{14}H_{12}O_8$, m.p. 246° (decomp.) [*K* salt, *Et* ester, m.p. 230—234° (decomp.), *Me*$_3$, m.p. 192°, *Et*$_3$, m.p. 172—174°, derivatives]. On acetylation the acid loses 1 mol. of H_2O forming the *Ac*$_2$ derivative, m.p. > 310°, of $C_{14}H_{10}O_7$. (I) and (II) also produce 6-methylsalicylic acid. The mycelium of (I) yields a cryst. N-containing *compound*, m.p. 165° (decomp.); and the mycelium of (III) a neutral *compound* $C_{40}H_{79}O_5N$, m.p. 132—135°. J. N. A.

Cultural factors necessary to determine the fertility of soil by means of *Aspergillus niger*, Cramer. A. Sartory, R. Sartory, J. Meyer, and F. Arnold (Compt. rend., 1935, **200**, 1692—1694).—The influence of K and P on the growth of *A. niger* (I) is determined in a culture medium of known composition. Low sugar (II) content and high p_H increase the sensitivity of moulds to P and K, whereas high (II) and N contents retard growth, the effect being greater for moulds other than (I). The medium must be dil. so that the constituents of the added soil other than K and P will not affect the yield of (I). J. L. D.

Serologically active (haptenic) carbohydrates of genotypes of *Neurospora tetrasperma* and *N. sitophila*. H. W. Wilcox and G. K. K. Link (Phytopath., 1935, **25**, 39).—Polysaccharides isolated from strains of these organisms gave positive precipitin reactions with rabbit's antisera. A. G. P.

Action of urinary growth-factors. Action on a micro-organism. W. H. Schopfer (Arch. Sci. phys. nat., 1934, **16**, Suppl., 200—203).—Extracts of dried human urine (I) by $COMe_2$, $CHCl_3$, abs. EtOH, 95% EtOH, H_2O, 50% $COMe_2$, and MeOH gave growths of *Phycomyces* increasing in order. (I) decolorised by C and pregnandiol were inactive. H. D.

Fermentation of rare sugars by members of the colon and aërogenes groups of bacteria. II. Cellobiose. C. F. Poe and D. E. Klemme (J. Biol. Chem., 1935, **109**, 43—46).—A table summarises the formation by *Escherichia coli*, *E. communior* and *politana*, *Aërobacter aërogenes*, and *A. cloacae*, when grown on a nutrient broth–cellobiose medium, of CO_2, H_2, volatile and non-volatile acids, EtOH etc. and curves show the changes of p_H. P. W. C.

Comparison of presumptive tests for the *coli-aërogenes* group of bacteria. I. V. Shunk (J. Elisha Mitchell Sci. Soc., 1934, **50**, 42—43).—*E. coli* and *A. aërogenes* produced gas in lactose–bile salt media containing brilliant-green, but not in those with crystal-violet or basic fuchsin. Gas production occurs with all 3 dyes if a certain fluorescent bacterium, capable of lowering the oxidation–reduction potential, is present. Ch. Abs. (*p*)

Soft rot and colon–typhoid–dysentery groups of bacteria. II. Physiology. A. R. Stanley (Phytopath., 1935, **25**, 34—35).—The customary physiological tests (sugar fermentation, NO_3' reduction, indole formation, etc.) are insufficient for sp. identification of these organisms. A. G. P.

Isolation of typhoid and paratyphoid bacilli from water. J. Szper (Compt. rend. Soc. Biol., 1935, **118**, 1675—1677).—The bacilli are isolated from large excesses of *B. coli* by growing in a medium containing conc. $Na_2S_4O_6$. R. N. C.

Action of sodium tetrathionate on the development of typhoid and paratyphoid bacilli. J. Szper (Compt. rend. Soc. Biol., 1935, **118**, 1677—1679).—$Na_2S_4O_6$ in high concn. inhibits growth of *B. coli*, but only retards that of typhoid bacilli as compared with their growth in bile medium. R. N. C.

Composition of a mineral medium particularly favourable for the growth of typhoid bacilli. Filtrates of typhoid bacilli cultivated on this medium; their mode of action; their utilisation in therapy. F. Le Chuiton, R. Pirot, C. Berge, and J. Pennaneac'h (Compt. rend. Soc. Biol., 1935, **119**, 71—73).—The composition of a modified Uschinsky medium for the growth of typhoid bacilli is given. The filtrates from typhoid bacterial cultures apparently contain no anti-virus; they produce allergic shocks in guinea-pigs and rabbits, and improvement in serious typhoid cases. R. N. C.

Types of specific carbohydrates in the cholera and cholera-like vibrios. R. W. Linton and B. N. Mitra (Proc. Soc. Exp. Biol. Med., 1934, **32**, 464—

468).—The majority of the vibrios contain polysaccharides (I) formed from an aldobionic acid consisting of galactose and glycuronic acid; this is condensed with galactose in the (I) of the cholera vibrios, and with arabinose in that of the non-agglutinating H_2O vibrios. A few strains contain a third (I) formed from glucose only. R. N. C.

Proteins and carbohydrates of the cholera and cholera-like vibrios. R. W. Linton and B. N. Mitra (Proc. Soc. Exp. Biol. Med., 1934, **32**, 468—473).—Two types of pseudoglobulins occur in the cholera and H_2O vibrios, respectively. The vibrios can be classified in several groups from their sp. protein and carbohydrate contents. R. N. C.

Existence in the *S* and *R* forms of *B. aertrycke* and *B. gaertner* of an enzyme that cleaves the "complete" antigen with liberation of the "residual" antigen. A. Boivin and L. Mesrobeanu (Compt. rend. Soc. Biol., 1935, **118**, 1671—1673).—The enzyme eliminates the fatty acids from the "complete" antigen of the *S* forms of both bacilli, liberating the non-toxic "residual" antigen. The enzyme is intimately associated with the bacteria, from which it cannot be separated by diffusion or autolysis; it attacks the antigen equally well whether the latter is enclosed in the bacteria or has been added to the medium, the optimum p_H being 7—8. It is not inhibited by NaF, but is destroyed by trypsin-kinase or by heating to 100° at p_H 7. (Cf. this vol., 665.) R. N. C.

Spectrum of diphtheria toxin. F. Ottensooser, A. Krupski, and F. Almasy (Biochem. Z., 1935, **277**, 314—319; cf. Coulter *et al.*, A., 1932, 969).—100 g. of the toxin (I) contain hæmochromogen (II) equiv. to 0·7 mg. of hæmatin. The spectrum of (II) (3400—6400 Å.) is very similar to that of C_5H_5N-(II), and exhibits a band at 4080 Å. There is no relationship between the (II) content of (I) and its toxicity or time of flocculation. W. McC.

Stabilisation and recovery of diphtheria antitoxin flocculated by the toxin. H. Goldie (Compt. rend. Soc. Biol., 1935, **118**, 1401—1403).—The antitoxin (I) is recovered from the flocculate by addition of 0·5% of CH_2O, followed immediately by 2% of $NH_2{\cdot}C_{10}H_4(SO_3Na)_3$, and adjusting to p_H 5 with 20% citric acid; (I) is pptd. with globulins, whilst the toxin remains in solution. The ppt. after washing is dissolved in aq. NaOH; the solution contains most of the (I) from the flocculate. (I) is stabilised by momentary contact with the CH_2O; prolonged contact or a more conc. CH_2O solution destroys it. R. N. C.

Fermentation-inhibiting substance produced by *B. coli*. N. Weinstock (Proc. Soc. Exp. Biol. Med., 1934, **32**, 556—559).—Fermentation of glucose, galactose, and dextrin by *C. diphtheriæ* is inhibited or retarded by broth in which *B. coli* has previously been cultivated. The inhibiting substance is relatively thermostable. R. N. C.

Comparative study of the content and composition of ash in a bacterial species and its virulence. C. Barber (Compt. rend. Soc. Biol., 1935, **118**, 1655—1657).—The ash content of pneumococci and streptococci is lower in the strains that are more pathogenic to mice; ash-Ca increases with pathogenic power, whilst other metals decrease. R. N. C.

Root nodule bacteria of leguminous plants. XVI. Effect of air content of the medium on the function of the nodule and on the excretion of nitrogen. XVII. Efficiency of different strains of clover nodule bacteria. A. I. Virtanen (J. Agric. Sci., 1935, **25**, 278—289, 290—296).—XVI. The rate of excretion of N from nodules (I) in sand cultures ∝ the supply of air to the roots. Submergence of roots in liquid media resulted in abundant growth of (I), but poor plant growth and small N excretion from (I). The plants had a low N content. (I) thus obtained were capable of fixing N when re-exposed to air. The N compounds excreted by (I) and also those assimilated by the plants are probably derived from the decomp. of proteins of (I).

XVII. Different strains of *Rh. trifolii* retained their characteristic sizes and N contents during a 3-year growth period. Inoculation of plants with a more efficient strain in the third year did not affect growth. A. G. P.

Hydroxylamine, hydrazine, and amide as intermediate products of nitrogen fixation by *Azotobacter*. D. Burk and C. K. Horner (Naturwiss., 1935, **23**, 259—260; cf. A., 1934, 1265).—< 3 mg. per litre of NH_2OH has no effect (higher concns. are toxic) on the respiratory exchanges during 38 hr. of *Azotobacter* in 21% O_2–79% H_2, although equiv. amounts of NO_3'-N or N_2 result in a doubling of the colony in 3—4 hr., which indicates that NH_2OH is not utilised. 0·1 mg. of NO_3- or NH_3-N per litre causes a max. growth, unaffected by concns. up to 5000 mg. of N per litre. N_2H_4 cannot be utilised, but HCN (< 1 mg. per litre) can. J. L. D.

Formation of hyponitrous acid as an intermediate compound in the biological or photochemical oxidation of ammonia to nitrous acid. II. Microbiological oxidation. A. S. Corbet (Biochem. J., 1935, **29**, 1086—1096).—Oxidation of $(NH_4)_2SO_4$ by soil micro-organisms can proceed thus: $NH_3 \longrightarrow NH_2OH \longrightarrow H_2N_2O_2 \longrightarrow HNO_2 \longrightarrow HNO_3$. Frequently oxidation ceases after about 5% conversion of NH_4 salt into NO_2'. NH_2OH has only a transitory existence at p_H 6 and above, but CaN_2O_2 is an important intermediate. Oxidation of NO_2' to NO_3' may be due to autoxidation in acid media. J. N. A.

Anaërobic decomposition of plant materials. III. Comparison of the course of decomposition of rice straw under anaërobic, aërobic, and partly aërobic conditions. C. N. Acharya (Biochem. J., 1935, **29**, 1116—1120).—Under aërobic (I), partly aërobic (II), and anaërobic (III) conditions, the relative rates of decomp., together with the amounts of protein formed, decrease in the order (I), (II), (III). Cellulose and lignin are more easily attacked under (II) than (III). In general, the results under (II) are intermediate between (I) and (III). Mild aëration under (III) gives an increase of H_2 with CH_4 and org. acids, whilst strong aëration increases the CO_2. J. N. A.

Action of bios on processes of putrefaction. K. Suchorukov and T. Epel-Bogoslovskaja (Compt. rend. Acad. Sci. U.R.S.S., 1935, **1**, 636—641).—Bios preps. from brewer's yeast stimulate multiplication of and proteolytic action by *B. subtilis* and *Proteus vulgaris*; no activation of proteases occurs. F. O. H.

Reduction potentials of bacterial suspensions. J. Yudkin (Biochem. J., 1935, **29**, 1130—1138).—A modification of Green's apparatus (A., 1933, 785) is used to measure the redox potentials (I) of *B. coli*, *B. alkaligenes*, and *Cl. sporogenes*. (I) falls with time and is unaffected by succinate; glucose and formate induce more negative (I). Enclosing the Pt electrode in a collodion sac produces no change in (I). (I) determined colorimetrically have little relation to those determined electrometrically, whilst electrolytic determinations in the presence of indicators (II) gave the same vals. as (II) alone. There is no correlation between the mode of life of the cultures studied and their (I). H. D.

Butyl alcohol–acetone fermentation in sugar media. H. Reynolds, H. D. Coile, and C. H. Werkman (Iowa State Coll. J. Sci., 1934, **8**, 415—426).—Seven strains of *Clostridium acetobutylicum* showed similar courses of fermentation. Use of H_2O-insol. proteins (ovalbumin, casein, zein) as sole sources of N in glucose media proved successful. Reported differences in fermentation results are due to factors not now recognised as significant. Ch. Abs. (*p*)

Preparation of the specific soluble substance from vaccinia virus. W. K. Ch'en (Proc. Soc. Exp. Biol. Med., 1934, **32**, 491—494).—The virus-infected tissue is suspended in 0·9% NaCl and autolysed under Et_2O for 7 days. The suspension is then centrifuged, filtered, and boiled for 5 min. at p_H 5·5; the ppt. is removed by centrifuge and the liquid boiled at p_H 8·0, filtered, and evaporated in vac. to 1/3 vol. The active material is pptd. with 1 : 1 EtOH–Et_2O, dried, dissolved in H_2O, dialysed, and finally purified by repeated pptn. with EtOH. The product has no antigenic properties. Similar products are prepared in small quantities from the normal tissue; they resemble the product from the virus culture chemically, but not serologically. R. N. C.

Negative stains in the demonstration of bacteria. R. W. Cumley (Stain Tech., 1935, **10**, 53—56).—Indian ink, nigrosine, induline, Congo-red, Poirier's blue, aniline-blue, China-blue, blue de Lyon, and night-blue are recommended. H. W. D.

Inhibition of growth of pollen and mould under *X*- and cathode-ray exposure. C. P. Haskins and C. N. Moore (Radiology, 1934, **23**, 710—719).—The incident energy required to inhibit mycelial growth in moulds by hard *X*-rays is 2·1× that for soft *X*-rays. The corresponding ratio for pollen is 6. Ch. Abs. (*p*)

Action of cinnamic acid in chloroform, of mercuric chloride, and of tincture of iodine on hyphomycetes. W. Aldick (Arch. Dermatol. Syphilis, 1934, **170**, 410—424; Chem. Zentr., 1934, ii, 3969—3970).—Comparative effects of these materials on the growth of *Trichophyton gypseum* are recorded. A. G. P.

Relation of action of chlorine to bacterial death. C. S. Mudge and F. R. Smith (Amer. J. Publ. Health, 1935, **25**, 442—447).—When milk in which bacteria had grown was treated for 3—10 min. with NaOCl the plates in which the action was stopped with $Na_2S_2O_3$ when plating gave a higher count than those in which it was not, and a 1 : 10 dilution gave higher results than the usual direct plate. When a mixture of H_2O and bacteria was chlorinated and plated and also run in several dilutions, a reduction of 99% was recorded on the plate, but virtually none by the serial tubes. C. J.

Effect of dilute solutions of certain antiseptics on the viability of tubercle bacilli. S. R. Douglas and P. Hartley (Tubercle, 1934, **16**, 97—99).—Data for PhOH and "merthiolate" are given. Results with CH_2O were inconclusive. Ch. Abs. (*p*)

Sterilisation by ultra-violet emissions from a high-tension lamp. E. Gilles (Compt. rend. Soc. Biol., 1935, **118**, 1440—1442).—The radiations kill young cultures without affecting the media. R. N. C.

Physiological production of sympathin in the liver. G. P. Whitelaw and J. C. Snyder (Amer. J. Physiol., 1934, **110**, 247—250).—Sympathin is liberated from the liver under such physiological conditions as those of the decorticate animal. R. N. C.

Action of pepsin on the succagogic and hypoglycæmic activity of secretin. J. La Barre and J. Ledrut (Bull. Soc. Chim. biol., 1935, **17**, 459—471).—By the action of pepsin on secretin and pptn. with $CCl_3{\cdot}CO_2H$ a substance, "incretin," is obtained having no succagogic, but considerable hypoglycæmic, activity when injected into normal rabbits and depancreatised dogs. A. L.

Purification of callicrein. F. Bischoff and A. H. Elliot (J. Biol. Chem., 1935, **109**, 419—427).—Purity 2—5 times that attained by Kraut *et al.* (A., 1932, 547) is reached by concn. of the urine in a vac., dialysis, pptn. with HCl, fractional pptn. with 75% EtOH saturated with NaCl, selective adsorption on $Zn(OH)_2$, elution with aq. $NaHCO_3$, and another fractional pptn. with EtOH, the p_H being maintained throughout within the limits of stability of the crude product. The purified material is unstable. W. McC.

Crystalline insulin. D. A. Scott and A. M. Fisher (Biochem. J., 1935, **29**, 1048—1054).—Ash determinations on different samples of insulin (I) (of original ash content of 0·02%) crystallised from NH_4OAc solutions with Zn, Co, or Cd showed const. vals. for the respective metals. The average ash content of each (I) salt was ∝ the at. wt. of the metal it contained, indicating that cryst. (I) contains the metals as chemically combined constituents. P. W. C.

Zinc content of bovine pancreas. A. M. Fisher and D. A. Scott (Biochem. J., 1935, **29**, 1055—1058).—Bovine pancreas (I) contained 20 mg. of

Zn per kg. of fresh tissue irrespective of the age of the animal from which the gland was obtained. The amount of Zn in (I) was thus many times that necessary to account for the available insulin (II) as the Zn salt, and the amount of (II) extractable did not bear any simple relationship to the Zn content of the (I). Co and Ni were not detected in (I). P. W. C.

Crystalline insulin. II. (Appendix.) E. Brüch (Arch. exp. Path. Pharm., 1935, **178**, 396; see A., 1934, 223).—The oxidation (I) of commercial insulin preps. by alkaline $K_3Fe(CN)_6$ (*loc. cit.*) is not related to their physiological activity, which, however, appears to be ∝ the difference in the vals. of (I) before and after inactivation. F. O. H.

Insulin. XIII. The sulphur of insulin. K. Freudenberg and T. Wegmann (Z. physiol. Chem., 1935, **233**, 159—171; cf. A., 1933, 321).—The activity of insulin (I) is diminished and/or destroyed by Na_2CO_3, cysteine (II), reduced glutathione, thioglycollic acid, thiolactic acid, leuco-methylene-blue, H_2S, H_2S_2, Na_2SO_3, HCN, CH_2:CO, ascorbic acid, quinol, I, BzO_2H, NaOH, or irradiation (III). If inactivation is not carried too far, reactivation (*e.g.*, with H_2O_2) is attained in some cases [(II), (III)]. In most or all of these actions the S·S group of (I) is involved. Inactivation by NaOH is accompanied by elimination of H_2S and a little NH_3. At p_H 7·4, $CH_2I{\cdot}CO_2H$ attacks (I) only slowly. The NH_2-N of (I) cannot be satisfactorily determined by Van Slyke's method because org. S compounds reduce HNO_2 to N_2. The products of the action of H_2S_2 on (I) are very toxic. The mol. wt. of (I) is 9000—18,000. W. McC.

Time curve after insulin. M. C. Hrubetz (Amer. J. Physiol., 1934, **110**, 384—386).—Blood-sugar in rats reaches its min. 1 hr. after injection of insulin, and after 3 hr. has risen again to a level < the initial level, where it remains steady, and this is the same level reached by the blood-sugar of rats starved for 6 hr. without insulin. There is no indication of a late hyperglycæmia in the injected animals. R. N. C.

Calcium in supersensitivity to insulin. H. Hundscheidt (Zentr. inn. Med., 1934, **55**, 369—371; Chem. Zentr., 1934, ii, 3519).—In cases of supersensitivity administration of Ca preps. permits satisfactory insulin therapy. A. G. P.

Effect of insulin on the purine metabolism of the Dalmatian coach dog. I. L. Chaikoff and P. S. Larson (J. Biol. Chem., 1935, **109**, 85—95).—Insulin increased the output of uric acid, but did not affect the excretion of allantoin. 1 hr. after injection of insulin, the blood-uric acid (I) began to increase, the max. effect after 10 units of hormone being obtained after 3 hr. When hypoglycæmia was inhibited by ingestion of glucose just before administration of insulin, (I) did not increase. P. W. C.

Effect of "chronic" experimental liver damage on the blood-sugar response to insulin. R. G. Sprague (Amer. J. Physiol., 1934, **110**, 488—489).—Dogs with Eck fistulæ are slightly more sensitive to insulin than normal dogs. R. N. C.

Modifications of gastric secretory activity under the influence of parathyroid extracts. J. La Barre and P. Destrée (Compt. rend. Soc. Biol., 1935, **118**, 1624—1627).—Injection of parathyroid hormone in dogs causes an increase in free and total HCl and mucus in the gastric secretion that reaches its max. at the 3rd hr. A series of injections at 3—4 day intervals causes a steady increase of mucus secretion. R. N. C.

Action of parathyroid hormone in normal and hypophysectomised pigeons. O. Riddle and L. B. Dotti (Proc. Soc. Exp. Biol. Med., 1934, **32**, 507—509).—Parathormone increases serum-Ca in normal, hypophysectomised, and thyroidectomised pigeons. R. N. C.

Evaluation of parathyroid hormone by means of sodium fluoride. M. Kochmann (Deut. med. Woch., 1934, **60**, 1062—1063; Chem. Zentr., 1934, ii, 3519).—The hormone counteracts the lethal dose of NaF or $H_2C_2O_4$ in mice. A. G. P.

Adrenal. VIII. Preparation of adrenal cortical hormone suitable for oral administration. A. Grollman, W. M. Firor, and E. Grollman (J. Biol. Chem., 1935, **109**, 189—200).—The aq. $COMe_2$ extract of pig cortical hormone (I) (A., 1933, 642) is chilled, lipins are removed, and the $COMe_2$ is distilled off. (I) is adsorbed on norit at p_H 7·0 and the norit–hormone prep. is washed with dil. HCl and NaOH, and assayed by feeding to adrenalectomised rats (II) and dogs. The same equiv. of gland is required to keep (II) in perfect health in oral charcoal feeding or intraperitoneal injection. H. D.

Cortico-adrenal influence on blood-sugar mobilisation. R. L. Zwemer and R. C. Sullivan (Endocrinol., 1934, **18**, 730—738).—Removal of the adrenal cortex (I) in cats has a more marked effect on blood-sugar (II) than removal of the medulla. The fall of (II) ∝ the time after removal of (I). Although (II) definitely decreases after complete adrenalectomy, it remains within the lower normal limit for some days. The low (II) is not due to depletion of reserves; it can be raised rapidly by excitement, adrenaline (III), cortin (IV), or (III) and (IV) mixed. The rate of rise and fall of (II) after injection of (IV) is < that after (III); the mixture produces a rapid rise and a slow fall. R. N. C.

Inter-relationship of the adrenal cortex and the anterior lobe of the pituitary. H. B. Shumacker, jun., and W. M. Firor (Endocrinol., 1934, **18**, 676—692).—Hypertrophy or atrophy of the pituitary (I) in the rat causes a similar change in the adrenal cortex (II). Removal of (I) destroys the capacity of (II) to undergo compensatory hypertrophy, whilst (II) insufficiency causes changes in (I). Removal of (I) and (II) lowers the rate of growth and body-temp., which in (I)-deficient animals cannot be restored by (II) hormone. Atrophy of the gonads after removal of (I) is not due to lack of (II) hormone, but that after removal of (II) is probably due to (I) degeneration. (I) transplants induce œstrus and premature maturity in adrenalectomised female rats. R. N. C.

Perfusion of adrenal gland with reference to mechanism of adrenaline stabilisation. R. D. H. Heard and A. D. Welch (Biochem. J., 1935, **29**,

998—1008).—A Ringer–Locke perfusate (I) of the adrenal of the ox contains pressor activity (II). Acetylcholine added to (I) gave no increased (II), eserine gave a slight increase; the adrenaline (III) output was increased by 150% by both drugs. (I) on shaking at 38° maintained their (II) const. for 3—21 hr., when (II) decreased fairly rapidly; the ascorbic acid (IV) content decreased continuously under these conditions. (III) added to (I) is similarly stabilised. No correlation exists between the amounts of (III) and (IV) secreted on perfusion. SH groups were absent from (I) both before and after reduction with Sn and HCl. The curves of O_2 uptake of (IV)+(III) and glutathione+(III) with time are characteristic of redox systems, and are similar to that of (I)+(IV). The presence of an inhibitor to the oxidation of (IV) in (I) is postulated and shown to exist in cell-free extracts of liver. H. D.

Adsorption by erythrocytes of substances in the blood, especially adrenaline. W. Bross and P. Kubikowski (Arch. exp. Path. Pharm., 1935, **178**, 212—228).—Adrenaline (I) is less rapidly destroyed in blood (II) than was previously believed. Thus (I) added to whole (II) retains most of its pressor action after 7 days at 0° and a little after 7 days at 37° with hæmolysed (II); with serum from bacterially decomposed (II) at 37°, no activity remains after 7 days. The methylene-blue technique (Euler, A., 1933, 986) gives acceleration with human serum and erythrocytes (III) at concns. of $\ll 1:400$ and 1 : 3200, respectively, indicating [(I)] in (II) of $3{\cdot}233\times10^{-11}$ g. per c.c. (cf. *ibid.*). The transport function of (III) for (I) and other hormones, toxins, etc. is discussed. F. O. H.

Effect of adrenaline on the purine metabolism of ordinary and Dalmatian dogs. I. L. Chaikoff, P. S. Larson, and L. S. Read (J. Biol. Chem., 1935, **109**, 395—404).—Subcutaneous injection of adrenaline (amounts insufficient to increase blood-pressure) into ordinary and Dalmatian (I) dogs causes increase in the urinary excretion of allantoin. In (I) urinary excretion of uric acid (II) also increases and the (II) content of the blood increases greatly. W. McC.

[Chemistry of] oxytocin. K. Freudenberg, E. Weiss, and H. Biller (Z. physiol. Chem., 1935, **233**, 172—173).—Acid hydrolysis of oxytocin (I) produces tyrosine, cystine, and small amounts of histidine, but these may be derived from impurities. (I) is destroyed by papain (II) (optimum at p_H 7) and by HCN-activated (II), which also destroys the SH groups. Trypsin and tyrosinase destroy (I) and BzO_2H, H_2O_2, alkali, and ultra-violet light (III) damage it, but it is only slowly attacked by cysteine (even at p_H 8·6) and scarcely affected by Na amalgam in aq. $NaHCO_3$. In neutral or alkaline solution it is rapidly, in acid solution only slightly, attacked by I. Neutral or alkaline aq. Na_2SO_3 and H_2 in presence of Pd rapidly attack it, but some of the activity is restored on subsequent treatment with H_2O_2. (I) differs from insulin in having a lower mol. wt. and in being less sensitive to attack by BzO_2H, H_2O_2, alkali, or (III), but more sensitive to attack by $CH_2{:}CO$. W. McC.

Action of posterior pituitary on blood-lactic acid. A. D. Marenzi (An. Farm. Bioquim., 1934, **5**, 18—24; Chem. Zentr., 1934, ii, 3518).—Prolonged intravenous injections of extracts of standard posterior pituitary powder into anæsthetised dogs increase blood-lactic acid if the dosage is > 1 mg. of powder per kg. per hr. A. G. P.

Comparative study of the effects of preparation of the posterior lobe of the pituitary gland on water interchange in frogs. F. R. Steggerda and H. E. Essex (Proc. Soc. Exp. Biol. Med., 1934, **32**, 425—428).—Posterior pituitary preps. cause an increase in wt. of frogs due to increased H_2O absorption. The effect of pitocin is > that of pitressin. Pitocin increases the rate of loss of H_2O when the frogs are kept out of H_2O. R. N. C.

Kidney as a site of thyroid action. K. Oberdisse and E. Roda (Arch. exp. Path. Pharm., 1935, **178**, 252—259).—The average vals. of Q_{O_2} for rabbit's liver, brain, and kidney (I) are 12·3, 10·3, and 12·7 c.c. per hr. per mg. dry-wt., respectively. That of (I) is increased by approx. 54% by injection of thyroxine (II), whilst denervation of the one (I) does not influence either its normal val. or the increase due to hyperthyroidism when compared with the other (I). The data indicate that (II) does not act through the nervous system, but on the peripheral tissues (cf. A., 1931, 1337). F. O. H.

Influence of thyrotropic hormone on blood- and organ-fats and -lipins, blood-sugar, diuresis, and excretion of sodium chloride and urea in rabbits. F. Rothschild and H. Staub (Arch. exp. Path. Pharm., 1935, **178**, 189—196).—Single or, to a greater extent, continuous intravenous injection of thyrotropic hormone produces changes in the blood-levels of petrol-sol. substances (but not in the I val.), and free and esterified cholesterol. The I val. of the depot-fat is increased. Hyperglycæmia and loss in body-wt. occur after large doses. Small doses tend to increase and large doses to decrease the urinary excretion of H_2O, NaCl, and urea (cf. A., 1933, 1209; 1934, 701). F. O. H.

Action of the thyrotropic substance of anterior pituitary origin on the thyroxine content of the blood. E. Zunz and L. La Barre (Compt. rend. Soc. Biol., 1935, **118**, 1622—1624).—Blood-thyroxine is increased by intravenous injection of thyrotropic hormone. R. N. C.

Carotenæmia in animals treated with thyroxine or thyrotropic hormone. Carotene in the adrenals after injection of thyroxine. C. I. Parhon and G. Werner (Compt. rend. Soc. Biol., 1934, **118**, 1659—1660).—Blood-carotene in the duck is decreased by injection of thyroxine or thyrotropic hormone. Thyroxine increases carotene in the adrenals. R. N. C.

Response of adult rat testes, sex accessories, and adrenals to injections of prolactin. O. Riddle, E. L. Lahr, R. W. Bates, and C. S. Moran (Proc. Soc. Exp. Biol. Med., 1934, **32**, 509—512).—Daily injections of prolactin in adult rats do not affect the wt. of the testes, but decrease that of Cowper's glands and increase that of the adrenals.

Follicle-stimulating hormone and prolan do not increase the wt. of the testes, even in relatively high doses. R. N. C.

Stability of prolan; its enzymic nature. H. VON EULER and B. ZONDEK (Skand. Arch. Physiol., 1934, **68**, 232—244; Chem. Zentr., 1934, ii, 3518).—Prolan (I) loses 50% activity on heating for 45 min. (with p_H 7—8) at the "crit. death temp." 62°. In this respect and in its inactivation by exposure to ultra-violet radiation (I) exhibits enzyme-like properties. A. G. P.

Human corpus luteum and progestin. J. P. PRATT (Endocrinol., 1934, **18**, 667—675).—The progestin content of the human corpus luteum is < that of the sow. R. N. C.

Œstrin and progestin content of the corpus luteum of the sow. C. A. ELDEN (Proc. Soc. Exp. Biol. Med., 1934, **32**, 515—516).—Progestin is max. in the early corpus luteum 6—7 days after rupture of the follicle, falling steadily after this period. Œstrin rises to a max. in the fully-formed corpus luteum. R. N. C.

Hormone of the corpus luteum. D. VAN STOLK and H. PÉNAU (Bull. Soc. Chim. biol., 1935, **17**, 472—484).—A review. A. L.

Effect of gonadotropic hormones during gestation and lactation. H. SELYE, J. B. COLLIP, and D. L. THOMSON (Proc. Soc. Exp. Biol. Med., 1934, **32**, 530—534).—The ovarian response of the pregnant rat to the gonadotropic hormones from pregnancy urine (I) and from the anterior pituitary (II) is > that of the non-pregnant rat, the increase persisting after birth if nursing is not allowed. In hypophysectomised rats (I) preps. produce only thæcal luteinisation (III), which is also produced in lactation (IV) and pregnancy together with granulosa (III). (II) preps. do not produce thæcal (III) during (IV). Neither (I) nor (II) preps. produce the ordinary uterine reaction during (IV). R. N. C.

Production of ovulation by gonadotropic extracts. L. E. CASIDA (Endocrinol., 1934, **18**, 714—720).—Folliculin does not produce ovulation (I) in rats or rabbits when injected alone, but it occurs after subsequent injection of luteinising hormone (II). Anterior pituitary extract produces (I) in some strains of rats when injected alone, and in all strains when combined with small quantities of (II); larger quantities of (II) inhibit (I) with formation of corpora lutea atretica. R. N. C.

Quantitative and qualitative response to distributed dosage with gonadotropic extracts. L. C. MAXWELL (Amer. J. Physiol., 1934, **110**, 458—463).—The potency of gonadotropic pituitary extracts is increased 50 times by distributed dosage and addition of Zn salts. Zn salts also increase the augmenting effect of the pituitary synergist on pregnancy urine extracts. R. N. C.

Pregnancy urine given by mouth to gonadectomised rats: its effect on spontaneous activity and on the reproductive tract. C. P. RICHTER (Amer. J. Physiol., 1934, **110**, 499—512). R. N. C.

Anti-gonadotropic substances. C. BACHMAN, J. B. COLLIP, and H. SELYE (Proc. Soc. Exp. Biol. Med., 1934, **32**, 544—547).—Chronic administration of gonadotropic extracts (I) from pregnancy urine or the pituitary in rabbits results in the formation of substances inhibiting their action. Sera from animals so treated produce passive resistance to (I) when injected into other animals. R. N. C.

Effect of ovarian hormone on the pituitary, thyroid, and adrenal glands of spayed female rats. D. H. ANDERSEN (J. Physiol., 1934, **83**, 15—25).—The atrophied endocrines are restored to the normal wts. at œstrus by amniotin; hypertrophy can be produced in the thyroid and adrenals. R. N. C.

Action of prolan and folliculin on the testicle. M. PEPE and C. VACCA (Boll. Soc. ital. Biol. sperim., 1934, **8**, 1782—1784).—Prolan causes premature maturity and testicular hypertrophy in young male rats, whilst folliculin produces testicular atrophy. R. N. C.

Experimental hyperplasia of the prostate. A. S. PARKES and S. ZUCKERMAN (Lancet, 1935, **228**, 925—928).—Injection of œstrone into immature rhesus monkeys results in (*a*) a diminution in the no. of true prostatic glands with a corresponding increase in the amount of fibromuscular stroma and (*b*) epithelial growth in the uterus masculinus. L. S. T.

Demonstration of œstrin in the blood of women. C. F. FLUHMANN (Endocrinol., 1934, **18**, 705—713).—Serum containing œstrin, injected into spayed female mice, produces a mucification of the vaginal mucosa. During the menstrual cycle serum-œstrin shows a max. at the middle of the interval, a secondary max. during menstruation (I), and min. just before and after (II). R. N. C.

Comparison of theelin prepared from stallion urine, human urine, and from theelol; colorimetric determination of theelin and theelol. G. F. CARTLAND, R. K. MEYER, L. C. MILLER, and M. H. RUTZ (J. Biol. Chem., 1935, **109**, 213—220).—Theelin (I) is obtained from stallion urine by extraction of the latter, acid to congo-red, with BuOH, washing the extract with aq. NaCl, concn. in a vac. to a brown oil, and thence by the method of Butenandt (A., 1930, 1480). (I) prepared thus is identical with that obtained from theelol and from human pregnancy urine. The Kober (A., 1931, 1195) colorimetric determination of (I) is modified slightly. H. D.

Synthesis of compounds related to the sterols, bile acids, and œstrus-producing hormones.—See this vol., 752.

Masculinising action of urine. P. GLEY (Compt. rend. Soc. Biol., 1935, **119**, 32—33).—Extracts of adult male urine provoke equally well comb-growth and the appearance of other secondary sex characteristics in capons. R. N. C.

Melanophore hormone in urine. S. KONSULOFF (Klin. Woch., 1934, **13**, 490—491; Chem. Zentr., 1934, ii, 3974).—The melanophore hormone content of the urine is considerably increased in pregnancy. R. N. C.

Discovery and significance of vitamins. F. G. Hopkins (Nature, 1935, **135**, 708—712). L. S. T.

Structure and physiological activity. J. Pryde (Nature, 1935, **135**, 713—716).—The structures of vitamins, hormones, and carcinogenic compounds are discussed. L. S. T.

[Examination of] vitamins in Wood's light. A. Karsten (Z. Vitaminforsch., 1935, **4**, 139—143).—The behaviour of vitamin-containing preps. in Wood's light is discussed and a suitable lamp described (cf. B., 1929, 291). F. O. H.

Spectrophotometry of vitamin-*A* colour test. E. Rosenthal and M. Weltner (Biochem. J., 1935, **29**, 1036—1038).—The purplish-red colour of the $SbCl_3$–pyrocatechol test for vitamin-*A* (A., 1934, 225) shows max. at 545 and 475 mμ within 10 min. of testing; with the guaiacol modification, the colour remains unchanged for several hr. with max. at 545 and 478 mμ. F. O. H.

Determination of vitamin-*A* in blood. E. Rosenthal and C. Szilárd (Biochem. J., 1935, **29**, 1039—1042).—The light petroleum extract from 10—30 ml. of blood is dried in a vac. in presence of Na_2SO_4 and the residue is treated with $CHCl_3$–$SbCl_3$–guaiacol reagent (cf. preceding abstract). The resulting colour is compared with 0·001% aq. $KMnO_4$ or the "grey solution" of Leitz. F. O. H.

Determination of vitamin-*A* with the Hilger vitameter equipped with a device for photographic recording. O. Notevarp (Biochem. J., 1935, **29**, 1227—1235).—Comparison is made between traces made by the light on photographic paper. Increased accuracy is obtained and satisfactory agreement found between the vitameter readings, spectrographic determinations of the absorption at 328 mμ, and the blue vals. A differential method for determining vitamin-*A* (I) in oils is described, depending on the destruction of the (I) by irradiation. F. A. A.

Vitamin-*A*-active substances in egg-yolk. A. E. Gillam and I. M. Heilbron (Biochem. J., 1935, **29**, 1064—1067).—Using chromatographic methods with spectroscopic control, the unsaponifiable fraction of egg-yolk, after a phase test separation of carotene from xanthophyll followed by adsorption of the latter on $CaCO_3$, has been shown to contain vitamin-*A* both by the $SbCl_3$ blue test and by the characteristic adsorption band at 328 mμ. The petroleum phasic carotenoids consist of kryptoxanthin (I) and β-carotene. By feeding fowls on a diet rich in maize, it has been possible to increase the (I) content of the resulting yolks, although the final val. was still small. P. W. C.

Antagonism between vitamin-*A* and thyroxine. I. Abelin (Z. Vitaminforsch., 1935, **4**, 120—128).—Administration of vitamin-*A* to rats diminishes the increase in basal metabolic rate due to thyroid preps. (I); the retardation in growth due to excess (I) is also largely counteracted. The antagonism depends on the opposing effects on cell-lipin metabolism and muscle-glycogenesis. F. O. H.

Relation of lipolysis in blood to the defence reaction of the animal organism under administration of different vitamins. K. Holm (Z. Immunitäts., 1934, **82**, 479—494).—Vitamin-*D* in small quantities increases lipolysis (I) and the bactericidal index, but lowers them in toxic overdoses. Vitamin-*A* increases (I) slightly. R. N. C.

Respiration of tissues containing varying amounts of vitamin-*A*. A. Chevallier and H. Roux (Compt. rend. Soc. Biol., 1935, **118**, 1348—1349).—No correlation was observed between the vitamin-*A* content and respiration of rat or guinea-pig liver. H. G. R.

Effects of vitamin-*A*-deficient diets on reproduction of sows. E. H. Hughes (J. Agric. Res., 1934, **49**, 943—953).—Pigs were unable to reproduce when fed for considerable periods on a no. of barley-containing rations, unless a supplement of cod-liver oil was given. When fed as sole source of vitamin-*A*, barley supplied insufficient -*A* for reproduction. Additional protein feeding (caseinogen) together with -*A* enhanced the action of the vitamin. A. G. P.

Relation of vitamin-*A* and its precursor to liver disorder and to resistance to infection. E. Schneider and E. Widmann (Klin. Woch., 1934, **13**, 1497—1502; Chem. Zentr., 1934, ii, 3521).—During complete avitaminosis in rats and guinea-pigs vitamin-*A* can be utilised and stored, but its formation from the pro-vitamin ceases. In thyrogenic liver disorders, -*A* consumption increases and the reserve is lowered. In this condition the ability to utilise and store -*A* increased 8-fold. Metabolism of -*A* is related to glycogen metabolism in the liver. A. G. P.

Growth, productivity, life period, and progeny of guinea-pigs receiving high dosages of yeast (vitamin-*B*). P. Marangoni (Boll. Soc. ital. Biol. sperim., 1933, **8**, 1753—1756; Chem. Zentr., 1934, ii, 3977).—Dosages of 8—10 g. daily of beer yeast produced no ill effects, even in pregnant animals. The live-wt. increases of the young were > those of control animals. Puberty was reached in 4—5 months. The second generation was productive, but the progeny did not live. A. G. P.

Vitamin-B_1 content of glutinous rice. J. P. Spruyt and W. F. Donath (Geneesk. Tijds. Nederl.-Ind., 1935, **75**, 502—514).—Black varieties of glutinous rice (ketan) have a larger -B_1 content than white varieties. Results obtained by the "hæmatocrit" method correspond well with those obtained from the bird (*Munia maja*) test. Vals. > 1·2 international units per g. have been found. The process of "puffing" (about 15 atm. pressure at 150—160°) entirely destroys the vitamin. P. G. M.

Antineuritic (B_1) vitamin content of "black" katjang idjoe (*Phaseolus radiatus*). J. P. Spruyt and W. F. Donath (Geneesk. Tijds. Nederl.-Ind., 1935, **7**, 601—602).—Black katjang idjoe has the same vitamin-B_1 content as the green variety. S. C.

Degradation of flavins by light. Synthesis of lactoflavin (vitamin-B_2) and other flavins. Sugar-like side-chain of lactoflavin.—See this vol., 760.

Micro-determination of vitamin-*C*. D. GLICK (J. Biol. Chem., 1935, **109**, 433—436).—The method is a refinement of that (I) of Birch *et al.* (A., 1933, 646). For extraction of the vitamin (II) and prep. and standardisation of the 2 : 6-dichlorophenol-indophenol solution (III) the procedure of Bessey *et al.* (A., 1934, 227) is adopted, 9% AcOH replacing $CCl_3 \cdot CO_2H$. (III) is placed in the burette. The amount of (II) determined is about one fiftieth of that determined by (I). W. McC.

Determination of vitamin-*C* with 2 : 6-dichlorophenol-indophenol. A. FUJITA and D. IWATAKE (Biochem. Z., 1935, **277**, 293—295).—$CCl_3 \cdot CO_2H$ (I) oxidises vitamin-*C* and decolorises the indicator. The procedure of Harris *et al.* (A., 1933, 541) is more accurate than that of Tillmans (A., 1932, 310), but (I) should be replaced by 2% aq. HPO_3. W. McC.

Colorimetric determination of vitamin-*C*. A. FUJITA, D. IWATAKE, and T. MIYATA (Biochem. Z., 1935, **277**, 296—304).—Ascorbic acid (I) (4 c.c. of solution containing 0·5—10·0 mg. per 100 c.c.) in 2% aq. HPO_3 is accurately determined by adding first 1 c.c. of a solution of 2 g. of Na_2WO_4 in 10 c.c. of dil. H_2SO_4, then 0·4 c.c. of 2*N*-NaOH, and comparing the blue colour produced with that of a standard. The reaction is sp. and not given by substances (*e.g.* in liver, lungs, kidney, adrenals, heart) [other than (I)] which reduce 2 : 6-dichlorophenol-indophenol. $\leq$ 0·003 mg. of (I) can be detected. W. McC.

Determination of glutathione and ascorbic acid in animal tissues. K. WACHHOLDER, K. ANDERS, and K. UHLENBROOCK (Z. physiol. Chem., 1935, **233**, 181—185; cf. this vol., 511).—The ascorbic acid (I) of the tissues (II) is iodometrically determined, after destroying the glutathione (III) with CH_2O and the (III) by subtracting the (I) val. from that obtained before addition of CH_2O, but since (I) is partly attacked by CH_2O, a correction must be applied. The CH_2O is added after deproteinisation and in concn. < that previously used. The (II) vals. agree with those of Binet *et al.* (A., 1934, 574). (II) contain also other material which consumes I. (III) interferes with determination of (I) by Tillmans' method. The (I) and (II) contents of the organs of the rabbit and dog are given. W. McC.

Antiscorbutic activity of ascorbic acid isolated from Japanese green tea. S. MARUYAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1935, **27**, 10—12; cf. A., 1934, 1416).—0·8 mg. per day of ascorbic acid derived from Japanese green tea, or 0·5 mg. from Natumikan (Japanese lemon) juice, cures scurvy in guinea-pigs. J. L. D.

Ascorbic acid in the pituitary gland. A. GIROUD, C. P. LEBLOND, and R. RATSIMAMANGA (Compt. rend. Soc. Biol., 1935, **118**, 1311—1312).—The ascorbic acid contents of the anterior lobe, pars intermedia, and posterior lobe of ox pituitary are 1·65, 2·01, and 0·55 mg. per g. of tissue, respectively. H. G. R.

Vitamin-*C* content and reducing power of normal and pathological urine. W. VON DRIGALSKI (Z. Vitaminforsch., 1935, **4**, 128—136).—The daily urinary excretion of vitamin-*C* (I) by healthy adults was 36—79 mg., average 50 mg. Higher vals. were given only after ingestion of diets very rich in (I). With children the val. was 16—30 mg. according to age, whilst it fluctuated considerably with various diseases. Breast-fed children receive large amounts of (I) from the mother. The highest [(I)] in urine observed was 0·0104%. F. O. H.

Catalytic oxidation of ascorbic acid. A. E. KELLIE and S. S. ZILVA (Biochem. J., 1935, **29**, 1028—1035).—Normal distilled H_2O, but not H_2O repeatedly distilled in glass or SiO_2 apparatus, contains sufficient Cu and Fe to catalyse the irreversible oxidation (I) of aq. ascorbic acid. Dehydroascorbic acid (II) is an intermediary in (I). Saturation of H_2O with O_2 has no marked effect on (I). (I) is inhibited by aq. extracts of liver, kidney, muscle, spleen, intestine, and by plasma, intact or hæmolysed erythrocytes (III), and 0·1*N*-NaCl, but not by leucocytes. With (III), there is an initial (I) which $\propto$ the amount of (III) added and does not occur with CO-treated (III). (II) is probably reduced in the organism before acting as vitamin-*C* (A., 1934, 1271). F. O. H.

Effect of vitamin-*C* on metabolism. F. STRIECK (Biochem. Z., 1935, **277**, 279—283).—In dogs, oral, subcutaneous, or intravenous administration of ascorbic acid (I) results in increase, lasting about 3 hr., in the O_2 consumption, the magnitude of the effect being independent of the dose (0·05—1·0 g.). Prolonged treatment has no cumulative effect. In healthy persons doses of 0·4—1·0 g. in some cases produce increases of short duration (up to 37%) in the basal metabolism (II); in other cases they have no effect. In diseased persons having increased basal (II) no further increase follows administration of (I) nor is the R.Q. affected. W. McC.

Effect of fluorine feeding on the storage of vitamin-*C* in the rat and guinea-pig. H. M. HAUCK (J. Agric. Res., 1934, **49**, 1041—1045).—Addition of 0·15% of NaF to the diet over a period of 3—5 weeks did not prevent normal storage of vitamin-*C* in the adrenals and livers of guinea-pigs and rats. A. G. P.

Spectroscopic analysis of vitamin-*D* in wool-fat. H. TÖPELMANN and W. SCHUHKNECHT (Z. Vitaminforsch., 1935, **4**, 111—120).—Vitamin-*D* is not detectable spectroscopically in ultra-violet-irradiated lanolin or other wool-fat preps.; hence, if present, the content is < 0·03%. F. O. H.

Effect of viosterol on the calcium content of dog's bile. K. K. JONES and G. H. LAING (Amer. J. Physiol., 1934, **110**, 471—476).—Viosterol raises bile-Ca and lowers bile-flow only when given in quantities large enough to increase definitely the blood-Ca. Bile-Ca is uniform when bile-flow and blood-Ca are normal. Total Ca excretion in bile under normal conditions is almost completely dependent on the vol. output. R. N. C.

Thyrotropic action of vitamin-*D*. N. GOORMAGHTIGH and H. HANDOVSKY (Compt. rend. Soc. Biol., 1935, **118**, 1616—1619).—Vitamin-*D* in dogs produces a hyperthyroidism which attains its max. at the 10th day, afterwards decreasing slowly until

at the 50th day it is < normal. The sensitivity of the blood-pressure to adrenaline increases and decreases with the thyroid function. R. N. C.

Vitamin-*E* and fertility of poultry. F. ENDER (Z. Vitaminforsch., 1935, 4, 106—111).—Administration of wheat-germ oil (0·17—0·18 g. per day) to fowls increases the yield of living chicks from the artificially incubated fertilised eggs. F. O. H.

Carbon dioxide assimilation [in plants]. J. FRANCK (Naturwiss., 1935, 23, 226—229).—The mechanism of the formation of dehydrochlorophylls is discussed, and the cycle of chemical and energy exchanges involved in the assimilation process and fluorescent phenomena of chlorophyll is examined. A. G. P.

Chlorophyll fluorescence and assimilation of carbonic acid. III. Effect of carbonic acid on fluorescence in living leaves. H. KAUTSKY and A. HIRSCH (Biochem. Z., 1935, 277, 250—260; cf. this vol., 263, 311).—When the assimilation (I) of CO_2 by green leaves (II) is restricted by reduction of temp. or addition of phenylurethane or HCN the fluorescence (III) on irradiation, which is otherwise of short duration, is prolonged and/or intensified, but, since increase (up to 1%) in the concn. of the CO_2 supplied to (II) has no appreciable effect on the duration or intensity of (III), no direct transfer of the light energy absorbed by the chlorophyll to free or bound CO_2 occurs. Very high (up to 50%) concns. of CO_2 unfavourably affect (I) and interfere with the usual course of (III). W. McC.

Kinetics of photosynthesis. E. C. C. BALY (Proc. Roy. Soc., 1935, B, 117, 218—239).—The following scheme is proposed for the cycle of reactions occurring in photosynthesis; (*a*) a chlorophyll-*a*–CO_2–H_2O complex (I) under the influence of light gives chlorophyll-*b* (II) and CH_2O, which polymerises to hexoses; (*b*) in a dark reaction (II) is reduced (by carotene?) to chlorophyll-*a* (III); (*c*), (III) combines with CO_2 and H_2O to form (I). Kinetic formulæ for the photostationary state thus set up account for the experimental results of various workers, on the effects of temp., CO_2 concn., total light intensity, relative intensities of red and blue light, irradiation with flashing light, and poisons, on photosynthesis by *Chlorella*. F. A. A.

Relation between chlorophyll content and rate of photosynthesis. W. E. FLEISCHER (J. Gen. Physiol., 1935, 18, 573—597).—The rate of photosynthesis by a strain of *Chlorella* is ∝ the chlorophyll content when the latter is varied by varying the Fe or N supply. The behaviour when the Mg supply is varied is more complex. F. A. A.

Chlorophyll *b*.—See this vol., 763.

Effect of age on assimilation of leaves. B. N. SINGH and K. N. LAL (Ann. Bot., 1935, 49, 291—307).—Assimilation (I)–age curves of wheat, linseed, and sugar-cane under optimum conditions show low vals. in the early stages, reaching a max. at the period of max. growth and maturity, and declining towards the senescent stage. With reduced [CO_2] equiv. to that of the atm. early vals. are maintained at a steady level throughout growth. The intensity of (I) is controlled by the H_2O status, the chlorophyll content of leaves, and by catalytic substances, *e.g.* K and Ca. Different stages of development are marked by changes in rates of (I). The age and development of leaves is an important internal factor controlling the intensity of (I) and its mechanism. A. G. P.

Transpiration and pressure deficit. I. F. M. HAINES (Ann. Bot., 1935, 49, 213—238).—The absorption of H_2O by cut branches, the upper ends of which are sealed in a pressure vessel, is inversely related to the pressure applied. It is also influenced by the previous history of the branch. The effect is due to alteration of the vols. of the leaf cells and to modified transpiration rates. A. G. P.

Translocation and growth balance in woody plants. W. E. LOOMIS (Ann. Bot., 1935, 49, 247—272).—In 2-year apple and poplar trees movement of carbohydrates and org. N compounds, but not that of ash constituents, is temporarily checked by phloem ringing. In all trees examined N occurs in the tops only in the org. form. The carbohydrate level in sprouting segments is > in those bearing active leaves with cambial growth, although photosynthetic activity precedes normal cambial development. Primary growth is preceded by accumulation of simpler forms of org. N. The latter are probably condensed to form protoplasmic proteins in the apical meristems or in the leaves, but not in the cambium. The polarity of sprout growth and rooting is discussed together with the activity of hormones. A. G. P.

Respiration of the roots of plants. H. LUNDEGÅRDH and H. BURSTRÖM (Biochem. Z., 1935, 277, 223—249; cf. A., 1933, 874).—The basal respiration (I) of the roots (wheat seedlings) is independent of the respiration (II) due to the anions (III) (Cl', NO_3') in the nutrient medium. For (I) the presence of free O_2 is essential, whilst (III) control the uptake of residual O_2. The formula for aërobic conditions holds also for anaërobic. Concns. of KCN which greatly restrict anaërobic (II) leave (I) unaffected. Other poisons (Co, Pb, Tl, Hg, Cu) exhibit sp. differences as regards their action on (I) and (II). Anaërobic uptake of (III) is accompanied by an oxido-reduction process in which C of the hexose mol. is converted completely into CO_2 without the intervention of free O_2. W. McC.

Effect of halogenated aliphatic compounds on the respiration of potato tubers. L. P. MILLER (Contr. Boyce Thompson Inst., 1935, 7, 1—17; cf. A., 1934, 1418).—The respiratory activity (I) of tubers was increased by exposure to the vapours of a no. of halogen derivatives of the aliphatic hydrocarbons. In all cases the CO_2 output was increased even when > lethal concns. were used. The following comparative effects are recorded for low concns.: alkyl iodides > bromides > chlorides, *n*-halides > *sec.*-halides, $C_2H_4Br_2$ > C_2H_4BrCl > $C_2H_4Cl_2$, ethylene compounds > ethylidene compounds, propylene bromide < trimethylene bromide, α- > β- > *iso*-butylene bromide. Of the four simplest alkylene bromides $C_2H_4Br_2$ is the most effective. Increased (I) under these conditions is associated with increased p_H of the expressed juices. A. G. P.

Analysis of the effect of phosphorus supply on transpiration ratio in plants. R. F. Williams (Austral. J. Exp. Biol., 1935, **13**, 49—66).—An increase in P supply from a low to a moderate amount reduced the transpiration ratio (I) (ratio of H_2O transpired to amount of dry matter formed) of Algerian oats (*Avena sativa*), but an additional supply had no further effect. Except for the earliest period, the reduction in the ratio is due to a decrease with treatment in the transpiration rate per unit wt. of plant dependent on (*a*) a decrease in the transpiration rate per unit wt. of leaf, and (*b*) a decrease in the leaf-wt. ratio during part of the life cycle. Increased P supply tends to raise (I) indirectly through an effect on growth, but this action is more than balanced by the previously mentioned effect on transpiration rate. A significant correlation was found between the relative transpiration rate per unit wt. of leaf and the N content of the leaves. W. O. K.

Growth-promoting substance as a factor in the formation of plant organisms. V. M. Katunski (Compt. rend. Acad. Sci. U.R.S.S., 1935, **1**, 661—667).—Application of growth-promoting factor (I) by contact with coleoptiles of *Avena* and *Zea mais* inhibits the regenerative cell-division by cut surfaces of succulent leaves and the formation of adventitious rootlets by *Vicia faba* in which the growing points of the roots have been removed. The action of (I) is thus mainly one of cell-elongation and depression of development of plant organs. F. O. H.

Indole-3-*n*-propionic acid as a growth hormone and the quantitative measurement of plant response. A. E. Hitchcock (Contr. Boyce Thompson Inst., 1935, **7**, 87—95).—The acid possesses the same ability as hetero-auxin to produce bending, proliferation, and rooting responses in plants. The effects vary with the concn. of active material used, the method of application, and the species of plant. Quant. measurements are described. Positive effects are produced by a no. of other org. substances examined. A. G. P.

Location of oxidase in the apricot. R. Samisch (Amer. J. Bot., 1935, **22**, 291—293).—In ripe apricots oxidase (I) activity is highest in the epidermis especially in stomatal guard cells. It is also high in cells surrounding the fibro-vascular bundles, but is absent from the vessels. Within the cells (I) is located in vacuolar sap, but not in the protoplast. A. G. P.

Nitrogen absorption [by plants] and aëration. J. W. Shive (New Jersey Agric., 1934, **16**, No. 5, 2—3).—The total yield of tomato plants in H_2O cultures was increased by aërating the medium, O_2 absorption by the roots being much greater at p_H 7 than at p_H 4. Plants in aërated media removed up to 60% more N than those unaërated, the effect being more marked on NH_4- than on NO_3-N. Poorer growth in the absence of aëration results from O_2 deficiency and not from CO_2 accumulation. Ch. Abs. (*p*)

Dehydrogenating enzyme systems in germinating seeds. I. H. von Euler and R. Weichert (Z. physiol. Chem., 1935, **233**, 81—86; cf. this vol., 263).—Chlorophyll-defective (I) can be distinguished from normal (II) barley seedlings after 1 day's germination by means of the fluorescence microscope. As regards changes in dehydrase content, (I), (II), and (I) and (II) which have been exposed to *X*-rays behave similarly, all exhibiting great decreases in the first few days of germination [donators from the seedlings and Na malate (III), citrate, and succinate]. The decrease is especially pronounced with (III). The catalase content of (I) is < that of (II). W. McC.

Influence of heavy water on plants. A. J. Ewart (Austral. J. Exp. Biol., 1935, **13**, 9—15).—Dil. heavy water (1—1·3 per 1000) exerts a weak but usually inhibiting action on the growth of non-chlorophyllous plants and bacteria and on the germination of oat seeds. In the case of chlorophyllous plants slight acceleration of growth may be observed. W. O. K.

Effects of radioactive mud on germination of seeds and growth of seedlings. L. Havas (J. Agric. Sci., 1935, **25**, 197—216).—Stimulation of germination and growth resulted from exposure of seed to a Hungarian radioactive mud, the effect being produced by direct contact or by exposure at a short distance from a large amount of mud. Prolonged exposure had a deleterious effect. Wheat seeds treated with vital stains respond to irradiation in a manner which is influenced by the stain. A. G. P.

Catabolism of fat and phosphatides in germinating soya beans. W. Zimmermann and A. Baumann (Fettchem. Umschau, 1935, **42**, 65—69).—Changes in content and character (acid and I vals.) of the total lipins and phosphatides during the germination of soya beans in sand, earth, or exposed to light, are described. Heavy soils delay growth (and may cause death) of the seedlings by restricting access of air. E. L.

Effect of nitrate-nitrogen on the carbohydrate metabolism of inoculated soya beans. F. S. Orcutt and P. W. Wilson (Soil Sci., 1935, **39**, 289—296).—Low [NO_3'] in the nutrient reduced the level of sol. sugars in the plant sap, probably as a result of protein formation. Intermediate [NO_3'] stimulated photosynthesis and increased nodulation and N fixation. Higher [NO_3'] decreased the sugar level in the sap, since photosynthetic capacity, under these conditions, became the limiting factor in protein formation. Nodules were fewer and smaller. A. G. P.

Dynamics of metabolism during the ripening process of the red currant. O. J. Sobolevskaja and R. C. Turetzkaja (Bull. Acad. Sci. U.R.S.S., 1934, 1341—1365).—During the formation of the green berry there is a steady production of protein and carbohydrates [largely polysaccharides (I)]. In the softening stage prior to colouring invert-sugar (II) is translocated rapidly from the leaves. In the final colouring stage the increasing (II) content is still further supplemented by decomp. of (I). The accumulation of sucrose (III) in the final stages of ripening is brought about by the cessation of decomp. of (III), and not by increased synthesis from glucose and fructose. A. G. P.

Formation of rubber and resin and their movement in plants. N. N. Kiseley, A. P. Osipov, and K. A. Kuzmina (Bull. Acad. Sci. U.R.S.S., 1934, 1367—1386).—Formation of rubber and resin (or at least their precursors) is photosynthetic. The subsequent transformation may continue in the dark. The flow of latex in darkness is > in light. Rubber is not a by-product, but plays a definite part in the metabolism of the plant. The rubber content of plants shows daily variations with max. in the afternoon. A. G. P.

Effect of long and short day and shading on nodule development and on composition of the soya bean. E. W. Hopkins (Soil. Sci., 1935, **39**, 297—321).—Plants exposed to short day periods had high starch (I) and N contents whether the NO_3' supply was high or low. With advancing age, accumulation of (I) in low-NO_3' plants increased and the N constituents contained a larger proportion of simpler compounds. Plants grown under long-day conditions had lower (I) and N contents, notably in stems. With a low NO_3' supply such plants showed declining carbohydrate (II) and increasing N contents with advancing age. Shaded plants contained less (II) and more N than the unshaded. The wt. of nodules produced relative to the total wt. of plants was decreased by high NO_3' supply, short days, and shading. A. G. P.

Two varieties of chromatin in the nuclei of *Lilium Martagon*. M. Lenoir (Compt. rend. Soc. Biol., 1935, **118**, 1554—1556).—The double coloration shown by every important nuclear chromatic body of *Lilium Martagon* at the points of contact with the karyoplasm and the cytoplasm indicates the presence of two physically or chemically different varieties of chromatin. R. N. C.

Inorganic composition of wheat grown in Eastern Australia. I. W. Dadswell (Austral. J. Exp. Biol., 1935, **13**, 33—42).—The total ash contents (H_2O-free basis) of wheats grown in Victoria and New South Wales are in general < comparable data for wheats grown outside Australia. W. O. K.

Changes in the carbohydrate content of wheat during hardening against drought. I. M. Vassiliev and N. G. Vassilieva (Bull. Acad. Sci. U.R.S.S., 1934, 1340).—Drought-hardening is effected by the temporary maintenance of plants with a reduced H_2O supply until the leaf-tips begin to die back (8 days). During this period the monosaccharide (I) content of the plant increases steadily, sucrose (II) increases at first and decreases later, and hemicellulose (III) decreases in the early stages, subsequently rising rapidly to vals. > those of untreated plants (*U*). The hardened plants, when again receiving normal supplies of H_2O, have permanently lower H_2O and (I) contents and more (III) than *U*. The (II) content falls somewhat immediately after rewatering, but subsequently rises > that of *U*. A. G. P.

Odorous substance of green tea. IV. Odorous substance of dark tea. S. Takei, Y. Sakato, and M. Ono (Bull. Inst. Phys. Chem. Res. Japan, 1935, **14**, 21—22; cf. this vol., 267).—Tea-leaf oil contains Δ^{α}-hexenaldehyde and Δ^{β}-hexenol (I) which are converted into *Δ^{α}-hexendi-Δ^{β}-hexenylacetal*, b.p. 110°/2 mm., and *di-Δ^{β}-hexenyl ether*, b.p. 228°. Drying affords a condensation *product*, b.p. 240° (3 : 5-*dinitrobenzoate*, m.p. 78°), of (I), which gives dark tea its characteristic odour. J. L. D.

Pigments of the Mendelian colour types in maize. Chrysanthemin from purple-husked maize. C. E. Sando, R. T. Milner, and M. S. Sherman (J. Biol. Chem., 1935, **109**, 203—211).—Purple maize husks are extracted with MeOH–HCl (I), the extract is cooled, filtered, and the pigment is pptd. with Et_2O. Chrysanthemin (II) is pptd. from dil. HCl solution with $Pb(OAc)_2$ and the product decomposed with (I). Purification of (II) is completed by formation of the picrate, decomp., and pptn. with Et_2O. Its identity is confirmed by comparison with a synthetic specimen. H. D.

Components of *Parmelia perlata*, Ach.—See this vol., 749.

Composition of *Salvia miltiorrhiza* (Chinese drug tan-shin).—See this vol., 754.

Saponin and sapogenin of *Chenopodium ambrosioides*, L.—See this vol., 754.

Constitution of miliacin.—See this vol., 753.

***Salicaceæ*. VIII. Distribution of glucosides in the *Salicaceæ*. IX. Physiological study of the glucosides.** J. Rabaté (Bull. Soc. Chim. biol., 1935, **17**, 439—446, 447—458).—VIII. The distribution of the glucosides, sucrose, salicoside, daphneflavonoloside, populoside, flavopurposide, salinigricoflavonoloside, salipurposide, *iso*salipurposide, piceoside, salidroside, and salireposide in various *Salicaceæ* is described.

IX. A criticism of the technique and results of Jowett and Potter (A., 1902, ii, 686) and of Weevers (Jahrb. wiss. Botanik, 1904, **39**, 229). Contrary to the results of the first named, the glucoside contents of the stems of male and female *S. purpurea* are almost the same. A. L.

Indian medicinal plants: *Tinospora cordifolia*, *Solanum xanthocarpum*, and *Fumaria officinalis*. G. P. Pendse and S. Dutt (Indian J. Med. Res., 1932, **20**, 663—670).—Extracts afforded by H_2O and org. solvents from the dried powdered plants are described. *T. cordifolia* contains a waxy substance, $C_9H_{14}O_5$, m.p. 173—174°, an EtOH-sol. substance (glucoside ?), m.p. 76—77°, and an intensely bitter principle; *S. xanthocarpum* KNO_3 (1·6—1·9%), sugars (1·6%), solanine, and an oxidising enzyme; *F. officinalis* sugars (8·2%) and traces of alkaloid. F. O. H.

Alkaloids of the Chinese drug "Chin-shih-hu."—See this vol., 764.

Alkaloids of *Senecio platyphyllus*, D.C.—See this vol., 764.

Localisation of alkaloids in ipecacuanha root. M. Wagenaar (Pharm. Weekblad, 1935, **72**, 513—517).—Staining of the alkaloids (I) by pptn. with $K_4Fe(CN)_6$ followed by $FeCl_3$ after washing out excess reagent, and microdialysis show that (I) is localised in the peripheral cells. The yellow ppt. obtained with picric acid or $K_2Cr_2O_7$ is due to proteins

which resemble gliadin or hordein in being sol. in aq. EtOH. S. C.

Sterol from *Pinus sabiniana*. O. Gisvold (J. Amer. Pharm. Assoc., 1935, 24, 290).—The non-saponifiable residue from the oil extracted from *P. sabiniana* contained a *sitosterol*, m.p. 137·5° (*Ac* derivative 127·5°). H. D.

Phytochemistry. CXI. Sterols from *Monarda fistulosa*. O. Gisvold (J. Amer. Pharm. Assoc., 1935, 24, 214).—The unsaponifiable fraction of oil from wild bergamot leaves yields a sterol, m.p. 130—131° (Ac derivative, m.p. 115—118°). Stigmasterol does not appear to be present. F. O. H.

Volatile oil of *Hyptis mutabilis*. H. W. Werner (J. Amer. Pharm. Assoc., 1935, 24, 289—290).—The presence of sabinene and caryophyllene is indicated in the steam distillate from *H. mutabilis*. H. D.

Oil of the rose mallow (*Hibiscus moscheutos* × *H. coccineus*) seed. C. Barkenbus and S. T. Thorn (J. Amer. Chem. Soc., 1935, 57, 728—729).—This oil (20%) closely resembles cotton-seed oil, containing the glycerides of oleic (33·12), linoleic (45·53), linolenic (0·06), and saturated (15·6%; mainly palmitic, some stearic, and traces of arachidic) acids, and 1·34% of unsaponifiable matter. R. S. C.

Constitution of fustin and of the wood of *Rhus succedanea*, L.—See this vol., 757.

Starch and related polysaccharides of certain hardwoods. I. Preparation and properties of oak and walnut starch. W. G. Campbell (Biochem. J., 1935, 29, 1068—1080).—A method is described for the quant. isolation of the starch of the sapwood of English oak and walnut. Wood-starch is an acid polysaccharide consisting approx. of 90% of anhydroglucose residues and of an aldobionic acid anhydride (probably glucose glycuronic acid anhydride) which may be partly methylated. The cell walls of oak-sapwood contain a polysaccharide chemically related to that of the cell contents. Wood-starch forms a suitable source of nourishment for the larvæ of *Lyctus* powder-post beetles. P. W. C.

Nitrogen of polysaccharide complex from *Chondrus crispus*. M. R. Butler (Biochem. J., 1935, 29, 1025—1027).—The polysaccharide (A., 1934, 1047) has a N content approx. 13% of that originally present in the plant. F. O. H.

[Composition of] the mucilage from psyllium seed (*Plantago psyllium*, L.). E. Anderson and M. Fireman (J. Biol. Chem., 1935, 109, 437—442).—The mucilage is a mixture of polyuronides composed of *d*-galacturonic acid combined with *l*-arabinose (I). Chains of *d*-xylose mols. (8—35) and an insol. unsaponifiable substance are united to (I). The ash contains K, Ca, Fe, PO_4'''. W. McC.

Nucleic acid of ergot. I. M. Gatty-Kostyal and J. Tesarz (Wiadomosci farmac., 1934, 61, 17—18, 31—32; Chem. Zentr., 1934, ii, 3509).—Ergot contains 1·4—1·6% P_2O_5 (I) (calc. on dry matter) distributed thus: lecithin (I), 0·096—0·118%; sol. (I), 1·01—1·14%; nuclein (I), 0·29—0·32%. A *substance* (N, 15·21%; P, 8·73%) of the nucleic acid type was isolated. H. N. R.

Origin of the gases in the float of bladder kelp. G. B. Rigg and B. S. Henry (Amer. J. Biol., 1935, 22, 362—365).—The interior of the float is probably free from bacteria, and the CO therein is a respiratory product. A. G. P.

Mineral nutrition in Victorian fruit trees. F. M. Read and C. E. Cole (J. Austral. Inst. Agric. Sci., 1935, 1, 33—34).—The effects of deficiencies of individual mineral nutrients on the growth of trees are described. The balance of nutrients is more important for growth than are the actual amounts present. Deficiency of one nutrient may result in relatively increased absorption of another, thus intensifying the unbalance. A. G. P.

Distribution of calcium in leafy vegetables. P. C. Hsü and W. H. Adolph (Chinese Med. J., 1935, 49, 325—327).—Determinations of Ca in inner (I) and outer leaves (II) of certain Chinese vegetable foods show that the Ca content of (II) is from 2 to 20 times that of (I). It is suggested that (II) should be used as food in cases of Ca deficiency. H. T.

Effect of some cations on the permeability of cells to water. E. C. D. Baptiste (Ann. Bot., 1935, 49, 345—366).—The permeability of discs of potato and carrot to H_2O is affected by cations in the order $K^{\cdot} > NH_4^{\cdot} > Na^{\cdot} > H_2O > Mg^{\cdot\cdot} > Ca^{\cdot\cdot}$. A. G. P.

Toxicity of aluminium to seedlings: action of certain ions in eliminating the toxic effects. W. S. Eisenmenger (Plant Physiol., 1935, 10, 1—25).—Org. salts of Al (tartrate, citrate) are toxic to maize, soya beans, and buckwheat, the effect increasing with the concn. applied. $Ca(OH)_2$ is the best corrective. $Ca(NO_3)_2$ is less effective. The acidity of the Al salts may be neutralised by KOH, but the toxicity is not so completely eliminated as by $Ca(OH)_2$. Optimum growth-p_H for plants in Al salt–alkali media varies with constituents of the mixture and the proportions in which they occur. Al salts of org. acids are more toxic to plants than are the free acids in solutions of the same p_H. A. G. P.

Physiological action of potassium on the vital processes of chlorophyll-containing and chlorophyll-free cells. J. Stoklasa (Věstn. czechoslov. Akad. Zemed., 1934, 10, 146—151; Chem. Zentr., 1934, ii, 3513).—Irradiation with β- and γ-rays from Ra and K preps. favours the production of new plant tissues, even during the night. A. G. P.

Relation of sugar content and odour of clarified extracts of plants to their susceptibility to attack by the Japanese beetle. F. W. Metzger, P. A. van der Meulen, and C. W. Mell (J. Agric. Res., 1934, 49, 1001—1008).—Plants of which clarified extracts had a fruity odour and a high reducing sugar content were the more susceptible to attack. A. G. P.

Relation of carbohydrate–nitrogen nutrition to disposition of apple to infection by *Erwinia amylovora*. G. K. K. Link (Phytopath., 1935, 25, 26).—Trees having relatively low carbohydrate (I), and high N contents were susceptible to infection,

whereas those having high (I) and low N were resistant. The susceptibility of the former was maintained throughout the season. A. G. P.

Catalase activity in relation to age and viability of sclerotia of the cotton root-rot fungus. C. J. King, E. D. Eaton, and C. Hope (J. Agric. Res., 1934, **49**, 897—902).—In macerated tissues of root-rot sclerotia (I) catalase activity (II) declines steadily with the age of the (I) until loss of germinative power becomes appreciable. High (II) in (I) of 5—8 weeks old indicates an "after-ripening" process resembling that in seeds. The age and vigour of (I) may be assessed on the basis of determinations of (II). Drying of (I) causes a rapid decline in (II). A. G. P.

Effect of crown rust on yield, water economy, and composition of oats. H. C. Murphy (Phytopath., 1935, **25**, 28—29).—Rust infection reduced yields and increased H_2O utilisation of oat plants. The composition of grain and husk was not affected, except for slightly increased protein and decreased N-free extractives. In the green plant the % of insol. solids, sol. and insol. ash and N, and the acid-hydrolysable material was increased and that of sol. solids, sucrose, glucose, dextrin, and (notably) fructose declined. A. G. P.

Carotenoid pigments of uredospores of wheat-stem rust and four of its colour variants. M. Newton, H. Johannson, and T. Johnson (Phytopath., 1935, **25**, 30).—Spectrophotometric examination of naphtha extracts of spores indicates the pigments to be carotenoid in character and in most cases to consist chiefly of carotene. Pigment production in normal is > in subnormal light. A. G. P.

Metabolism of crown gall and hairy-root bacteria and the composition of crown galls. H. A. Conner, A. J. Riker, and W. H. Peterson (Phytopath., 1935, **25**, 11).—In aërated yeast-infusion media crown gall bacteria convert 2% of the glucose fermented into CO_2 and 10—15% into bacterial gum. For hairy-root bacteria the vals. were 20 and 10%, respectively. Small amounts of AcOH and $AcCO_2H$ were also formed. Fresh tomato and raspberry galls contained larger proportions of ash and total N, but less cellulose, starch, pentosans, and sugar, than did contiguous healthy tissue. Differences in α-NH_2-, amide-, NH_3-, NO_3'-N, or uronic acid content were insignificant. A. G. P.

Pathogenic bacteria which induce cell stimulation in plants. J. A. Pinckard (Phytopath., 1935, **25**, 31).—Five species of bacteria causing galls or overgrowths on plants were examined. The optimum growth temp. in all cases approached 28° and the growth produced varied with the C and N sources. Where starch or salts of org. acids were utilised alkalinity developed, whereas other C sources induced acidity. All cultures became acid when N was supplied as oxamide, *l*-tyrosine, or *l*-cystine. Highly reduced potentials occurred in undisturbed liquid cultures. A. G. P.

Chemical splitting of the tomato "combination-streak" virus complex. M. Shapovalov (Phytopath., 1935, **25**, 33).—Partial differentiation of the components of the complex is obtained by treating infected tomato or tobacco juice with $CoSO_4$, $NiSO_4$ or $ZnSO_4$ at concns. < those producing lytic effects on the whole complex. The two viruses showed relative differences in inactivation by these salts. A. G. P.

Influence of nutrition on host susceptibility to yellow tobacco mosaic. E. L. Spencer (Phytopath., 1935, **25**, 33—34).—Rapidly growing plants were less susceptible than those retarded by excessive N, or excessive P. Susceptibility was high in plants receiving small amounts of K and decreased sharply with increasing supplies of K. Growth retardation was not apparent until the amount of K given was very large. A. G. P.

Effect of proteoclastic enzymes on purified preparations of tobacco mosaic virus. A. F. Ross (Phytopath., 1935, **25**, 33).—The virus was inactivated by trypsin (I). Heating the digests at 70° for 20 min. resulted in recovery of most of the virus. Permanent inactivation (II) did not occur when enterokinase, $CaSO_4$, $CaCl_2$, $(NH_4)_2SO_4$, $MgSO_4$, and $BaCl_2$ were used as activators for (I). A combination of pepsin and (I) was less effective than (I) alone. Papain and cultures of certain bacteria caused (II). (I) attacked no protein which could be associated with the virus. A. G. P.

Factors affecting "longevity" *in vitro* of viruses of tobacco mosaic and of tobacco ring spot. B. M. Duggar and D. F. McAlister (Phytopath., 1935, **25**, 15).—The survival of mosaic virus in tobacco extract is favoured by condensation of the extract at low pressure and temp. and by addition of low (antiseptic) concns. of EtOH. The ring-spot virus is similarly affected by EtOH and by additions of buffer solutions of p_H 5·8—7·0, PO_4''' buffers being more favourable than citrates. A. G. P.

Factors influencing the activity of tobacco mosaic virus preparations. A. W. Petre (Contr. Boyce Thompson Inst., 1935, **7**, 19—28).—Improvements in the Vinson and Petre Pb-pptn. method (A., 1931, 1201) for preparing the virus are described. The susceptibility of plants to infection is influenced by the relative succulence of growth, but not by the rate of leaf expansion. A. G. P.

Culture vessel. H. S. Holden (Ann. Bot., 1935, **49**, 401).—A shallow culture dish is fitted with a conical flask-like cover. Cultures of micro-organisms, algæ, liverworts, etc. can be maintained for an extended period. A. G. P.

Reaction vessel for measurement of micro-biological gas metabolism. A. Janke and S. Kropacsy (Biochem. Z., 1935, **277**, 268—272).—Reactions (I) (*e.g.*, oxidation of EtOH by acetic bacteria) proceeding in the vessel described can be stopped at any desired point, the contents (liquid and gaseous) can be micro-chemically examined, and, if no gas is produced during (I), the rate of consumption of gases can be followed. W. McC.

Units of measurement in morphological technique. E. Agduhr (Z. Vitaminforsch., 1935, **4**, 136—139). F. O. H.