# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

JUNE, 1936.

## General, Physical, and Inorganic Chemistry.

**Excitation of the hydrogen lines $H_\alpha$, $H_\beta$, $H_\gamma$ by ultra-short electric waves.** H. Nagaoka and T. Mishima (Proc. Imp. Acad. Tokyo, 1936, 12, 1—3).—Excitation of $H_2$ in an electrodeless tube by means of 20-cm. waves, obtained from a magnetron, or for higher power a triode, is described. The method produces a steady excitation, without the presence of the Stark effect, and the fine structure of the lines can be readily photographed. A. J. M.

**Limits of the continuous spectrum and line intensities for helium.** H. O. Jancke (Z. Physik, 1936, 99, 169—188).—Spectral and probe electron energy measurements in the plasma of the He discharge indicate exchange interaction of highly excited neutral atoms with electrons in addition to ordinary recombination. A. B. D. C.

**Paschen–Back effect. III. $^2S^2P$ multiplets in strong fields. IV. Mutual spin-orbit interaction in two-electron spectra.** J. B. Green and R. A. Loring (Physical Rev., 1936, [ii], 49, 630—632, 632—634; cf. A., 1934, 137).—III. The theory is discussed and verified experimentally. The $^2S^2P$ multiplet of Li $\lambda$ 6708 was resolved in reversal and showed the fine structure predicted but not previously observed.

IV. Investigations for the Be triplet $\lambda$ 3321 $^3P^3S$ gave patterns in good agreement with calculations which take account of the interaction between the spin of one electron and the orbit of the other. N. M. B.

**Magnetic moment of $^6_3$Li.** H. Schüler and T. Schmidt (Z. Physik, 1936, 99, 285—287).—Assuming the mechanical moment to be 1, the magnetic moment is 0·6 nuclear magnetons. A. B. D. C.

**Magnetic moment of the $^7$Li nucleus.** J. H. Bartlett, jun., and J. J. Gibbons, jun. (Physical Rev., 1936, [ii], 49, 552).—The val. calc. from wave functions for Li is 4·58, disagreeing with 3·28 and 3·20 as calc. from experimental data (cf. Fox and Rabi, this vol., 1). N. M. B.

**Absorption spectra of oxygen due to interaction forces. I. Absorption bands of the $(O_2–O_2)$ molecule.** H. Salow and W. Steiner (Z. Physik, 1936, 99, 137—158).—Bands observed between 6299 and 3150 A. have been ascribed to $(O_2–O_2)$ mols. or collision pairs; they have been so allocated because of the variation of their shape and intensity with pressure between 40 and 160 atm., and foreign gas pressures up to 100 atm. A. B. D. C.

**Stark effect in neon.** W. Steubing and H. Kindler (Z. Physik, 1936, 99, 103—108). A. B. D. C.

**Mean lifetime of metastable neon atoms.** E. W. Pike (Physical Rev., 1936, [ii], 49, 513—515).—The concn. as a function of illumination intensity of excited atoms in the Townsend discharge in Ne, illuminated with red light from an auxiliary discharge in Ne, is computed from the electronic properties of Ne. The mean lifetimes of the metastable and resonance states are evaluated by comparison with direct measurements. N. M. B.

**Penning's "new photo-effect" in pure neon.** E. W. Pike (Physical Rev., 1936, [ii], 49, 515—518; cf. preceding abstract).—The maintaining voltage of a Townsend discharge in pure Ne, measured as a function of the illumination of the discharge with light from a Ne arc, was, in contrast to the case for slightly impure Ne, almost insensitive to illumination over a wide range of pressure, current, tube form, and cathode material. With progressive cleaning of the gas the change in maintaining voltage passed from a small positive val. through zero to a small negative val. N. M. B.

**Extinction of fluorescence of sodium.** V. Kondrateev and M. Siskin (Physikal. Z. Sovietunion, 1936, 8, 644—666).—The effect of various gases (A, $N_2$, NO, and $O_2$) on the extinction of the *D* fluorescence of Na has been investigated. The effective cross-section, characteristic of the extinction capacity, of A was independent of the energy ($\epsilon$) of the Na atoms within wide limits. In the case of $N_2$ and NO there is dependence on $\epsilon$ which is connected with the existence of two types of photochemical breakdown of the NaI vapour used for the fluorescence. The greatest extinction effect is given by NO and $O_2$; this is not connected with the fact that with these mols. there is a resonance between the vibrational energy of the mols. and the energy of electron excitation of Na, but it is suggested that the principal factor determining the effectiveness of a gas in extinguishing the fluorescence is the chemical force of interaction between the mols. A. J. M.

***A*-Bands of sulphur.** E. Olsson (Z. Physik, 1936, 99, 114—118).—Predissociation limits were observed at 2825 A. Odd rotation levels are absent from the ground state, indicating zero nuclear spin. A. B. D. C.

**Polarisation of resonance radiation from calcium and the effect of weak magnetic fields.**

A. Steinhäuser (Z. Physik, 1936, 99, 300).—Corrections (cf. A., 1935, 1183). A. B. D. C.

**Na I-like spectra of the elements titanium to copper (Ti XII—Cu XIX).** B. Edlén (Nature, 1936, **137**, 531—532).—Using an improved vac. spark spectrograph, the outstanding lines of the K I- and A I-like spectra have been revealed in the spectra of the elements from Ti to Zn XII and XIII. Lines belonging to Na I-, Mg I-, and Al I-like spectra have also been identified, those of Na I being the most intense and complete. The two most persistent transitions $3d^2D—4f^2F$ and $3p^2P—4d^2D$ have been traced through Cu XIX. L. S. T.

**Iron arc spectrum in the infra-red.** N. R. Tawde and V. S. Patankar (J. Univ. Bombay, 1935, 4, Part II, 65—69).—66 lines of the Fe arc in air have been measured in the region 7937—10,216 A. and compared with previous data. J. W. S.

**Spectroscopic investigation of discharges at high gas pressure.** W. W. Watson and G. F. Hull, jun. (Physical Rev., 1936, [ii], **49**, 592—596).—Spectra of high-energy discharges between Cu, Al, C, Mg, In, and Be electrodes in $N_2$, $O_2$, $H_2$, and He at pressures up to 15 atm. were examined at high dispersion. With the continuous spectrum background, absorption bands due to AlH, MgH, BeO, and CN were observed. Data for broadening and shift, in each case to the red, and for the pressure-broadening of the Al resonance lines are given. The breadths and shifts of the emission lines are attributed mainly to interat. Stark effect and slight resonance broadening, and the contours and pressure shifts of the self-reversals correspond with those due to van der Waals forces between Al atoms and gas mols. N. M. B.

**Polarisation of the radiation $\lambda = 2139$ A. emitted by optical resonance of an atomic beam of zinc.** P. Soleillet and S. Nikitine (Compt. rend., 1936, **202**, 1046—1047).—In a magnetic field of 0·53 gauss in the direction of the exciting ray 2139 A. the radiation emitted by an at. beam of Zn at right angles to the exciting ray is 74% polarised. R. S. B.

**New system of bands of $Se_2$ in the red.** B. Rosen and F. Monfort (Bull. Acad. roy. Belg., 1936, [v], **22**, 215—218).—The new system, ranging from 16,706—14,842 cm.$^{-1}$, has the same upper level as the principal system $^1\Sigma - ^2\Sigma$. The lower level is at approx. 9250 cm.$^{-1}$ above the normal of the $Se_2$ mol. A. J. M.

**Spectrum of selenium in the red and photographic infra-red.** B. Rosen and F. Monfort (Physica, 1936, **3**, 257—265).—The emission bands on the long-λ side of the main $^1\Sigma - ^1\Sigma$ system of $Se_2$ have been investigated. The results are discussed in relation to the heat of dissociation of $Se_2$. A new band system in the red is recorded. L. J. J.

**Origin of the broad bands in selenium and tellurium vapours.** B. Rosen, M. Désirant, and L. Neven (Nature, 1936, **137**, 498).—Broad bands observed in the absorption spectra of $Se_2$ and $Te_2$ for temp. up to 1000° confirm the interpretation previously given (A., 1935, 1291). L. S. T.

**Fluted bands of tellurium vapour.** M. Désirant and A. Minne (Compt. rend., 1936, **202**, 1272—1273).—The broad bands of $Te_2$ at λλ>5250 A. consist of two series extending to 6100 A. and 6500 A., respectively. The bands are due to transitions between an electronic state with an ill-defined min., and the higher vibrational levels of the ground state. L. J. J.

**Magnetic moment of the nucleus and hyperfine structures in the spectrum of doubly ionised antimony; structure of the arc line 3723.** J. S. Badami (J. Univ. Bombay, 1935, 4, Part II, 86—93).—The hyperfine structures of two doublets of the Sb III spectrum have been measured. After reclassification of the terms of this spectrum by interchanging $6s^2S$ and $5s5p^{22}S$ terms, a val. of approx. 2·7 proton-magnetons is obtained for the magnetic moment of the $^{121}$Sb nucleus. The structure of the 3723 A. line is interpreted, taking the mechanical moment of the nucleus as $(5/2)h/2\pi$ for both isotopes. J. W. S.

**Spectrum of doubly-ionised antimony.** S. G. Krishnamurty (Indian J. Physics, 1936, **10**, 83—90).—The analysis of the spectrum of Sb II due to Lang and Vestine (A., 1933, 2) has been modified and extended. A. J. M.

**Nuclear spin of iodine from the spectrum of $I_2$.** L. A. Strait and F. A. Jenkins (Physical Rev., 1936, [ii], **49**, 635; cf. Tolansky, this vol., 262).—Measurements of the alternating intensities in the mol. spectrum confirm the val. 5/2 for the nuclear spin. N. M. B.

***F*-Terms of Ce IV.** R. J. Lang (Physical Rev., 1936, [ii], **49**, 552).—Preliminary data for the terms are given. N. M. B.

**Hyperfine structure of platinum isotopes. I. Isotopes of platinum and their centre of gravity.** (Frl.) B. Jaeckel and H. Kopfermann (Z. Physik, 1936, **99**, 492—502).—Four isotopes, 194, 195, 196, and 198, are present in the intensity ratio 10 : 9 : 7 : 2. $^{195}$Pt has mechanical moment ½. A. B. D. C.

**Effect of added inert gas on the high-pressure mercury discharge.** W. Elenbaas (Physica, 1936, **3**, 219—236).—The extra energy loss is due to an increase in heat conduction caused by the presence of inert gas atoms. L. J. J.

**Zeeman effect of the hyperfine structure components of the mercury resonance line 2537 A.** A. Zvironas (Nature, 1936, **137**, 531). L. S. T.

**Application of the theory of the coherence of vibrations.** P. Soleillet (Compt. rend., 1936, **202**, 1167—1168).—Theoretical. Polarisation of some excited Hg lines is considered. M. S. B.

**Theory of pressure-broadening of spectral lines.** E. Gora (Proc. Indian Acad. Sci., 1936, **3**, **A**, 272—284).—Coupling between the energy levels of excited atoms and the virtual oscillators which determine the dispersion of the perturbing gas leads to a relation between the refractive index of the latter and the red shift of spectral lines. Other interactions affect width and violet shift. L. J. J.

**Pressure effects in band spectra.** H. Margenau (Physical Rev., 1936, [ii], **49**, 596—597).—

A simple theory of pressure effects due to foreign perturbing mols. without permanent polarity shows that shift and broadening are similar to those in the case of at. lines as a result of van der Waals interactions. Calculations and formulæ for models of a rigid rotator and simple harmonic oscillator show that the effects are almost independent of vibrational and rotational quantum nos. N. M. B.

**Mechanism in the positive column of a discharge.** L. S. Ornstein, H. Brinkman, and T. Hamada (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 315—324).—Theoretical. The shapes of the intensity curves for the bands of $N_2$ and $N_2^+$ over the tube radius are discussed. R. S. B.

**Λ-Type doubling in ${}^3\Pi$ states of diatomic molecules intermediate between Hund's cases *a* and *b*.** M. H. Hebb (Physical Rev., 1936, [ii], **49**, 610—618).—Mathematical. N. M. B.

**Temperature of helium in the high-frequency discharge.** J. Roig (Compt. rend., 1936, **202**, 1044—1046).—The temp. of He at 0·57—0·93 mm. in a high-frequency discharge running at 1760—2160 volts with $\lambda = 14$ m. is 187—250° as measured by an air thermometer. Calc. and observed interferometric measurements agree approx. R. S. B.

**Helium–tungsten arc.** O. Stübing (Helv. phys. Acta, 1935, **8**, 165—196; Chem. Zentr., 1935, ii, 980).—Relations between current, voltage, arc length, and pressure have been investigated between 11 and 500 mm. pressure. J. S. A.

**Preliminary stages of spark formation in various gases by the use of the Wilson chamber.** U. Nakaya and F. Yamasaki (Proc. Roy. Soc., 1936, **A**, **153**, 542—554).—Using a modification of the previous apparatus (A., 1935, 557), cloud photographs have been taken of sparks in $N_2$, $O_2$, $CO_2$, $H_2$, NO, and in air mixed with small amounts of org. vapours. The form and structure of the preliminary discharge are different for different gases, each gas showing a characteristic feature peculiar to itself. L. L. B.

**Production of metallic spectra by shock waves.** H. Muraour and A. Michel-Levy (Compt. rend., 1936, **202**, 949—950).—Line spectra of various metals were excited by the passage of a shock wave from the detonation of a mixture of $C(NO_2)_4$ and PhMe through A containing the metal or its oxide in suspension. They resembled the spark spectra. H. J. E.

**Structure of the spark striking to the surface of a solution.** P. Jolibois (Compt. rend., 1936, **202**, 400—402; cf. A., 1935, 831).—When a spark is passed between a Pt electrode and aq. $CuSO_4$ (10%) with the Pt positive, the latter becomes very hot, and the spectrum contains only the first and second negative bands of $N_2$ and the 3064 A. $H_2O$ band. With the Pt negative, the latter is less heated and a spectrum of $N_2$ is obtained throughout the length of the spark, the Cu spectrum from near the liquid, and a very intense H spectrum, containing the $H_\alpha$ and $H_\beta$ lines and the secondary H spectrum, from a luminous spot on the electrolyte. The observations suggest that the positively charged $H_2$ at the surface of the liquid forms the electrode and causes the pptn. of $Cu(OH)_2$ on passage of the current. J. W. S.

**Broadening of the lines in the radiation from hissing arcs.** T. Peczalski (Compt. rend., 1936, **202**, 1040—1042; cf. this vol., 438).—With increased evaporation of fused salt in contact with the anode of a C arc the arc hisses and the spectral lines for NaCl and $CaCl_2$ are wider than for a silent arc, the concn. of vapour being increased 20 times. R. S. B.

**Rapid measurements of probe characteristics of a gas discharge by means of oscillograph tubes.** J. Dürrwang (Helv. phys. acta, 1935, **8**, 333—369; Chem. Zentr., 1935, ii, 1138).—Dynamic characteristics of arc discharges have been investigated. The introduction of volatile salts (*e.g.*, Na or Cu halides) into a C arc produces alterations in the discharge which may be correlated with the ionisation potential of the metal. J. S. A.

**Electric arcs with liquid positive pole.** M. Pierucci (Nuovo Cim., 1935, [ii], **12**, 1—3; Chem. Zentr., 1935, ii, 1138).—A short arc may be struck between a C electrode and the surface of an aq. electrolyte. With a.c., a rectifying action is observed, the electrolyte functioning as positive pole only. The arc spectrum comprises the continuum of the electrodes and the gas lines, with the Balmer H lines when $H_2SO_4$ solutions are used. With shallow liquid layers the arc may strike through to the containing graphite crucible, then emitting strongly the spectra of the dissolved electrolytes. J. S. A.

**Evaluation of ultra-violet solar radiation of short-wave lengths.** W. W. Coblentz and R. Stair (Proc. Nat. Acad. Sci., 1936, **22**, 229—233).—A summary of recent experimental investigations and results. N. M. B.

**Bright line spectrum of Nova Herculis.** F. L. Whipple and (Miss) C. P. Gaposchkin (Proc. Nat. Acad. Sci., 1936, **22**, 195—200).

**Spectra of early-type stars in the near ultra-violet region.** P. Swings and M. Désirant (Astrophys. J., 1936, **83**, 31—46).—The spectra of three *B* and eleven *A* stars have been measured for λλ between 3570 and 3930 A. The behaviour of the elements is discussed. L. S. T.

***K*-Series for aluminium, manganese, and sodium.** V. Kunzl (Z. Physik, 1936, **99**, 481—491).—New lines have been observed in α and β groups (cf. A., 1935, 1292). A. B. D. C.

**Excitation potential, relative intensities, and wave-lengths of the $K\alpha''$ *X*-ray satellite line.** L. G. Parratt (Physical Rev., 1936, [ii], **49**, 502—507).—Data and ionisation curves of the line are given for S (16) to V (23). The excitation potential is 4070 ± 250 volts, and the line is attributed to a $KM \rightarrow LM$ transition. The relative intensity $K\alpha''/K\alpha_1$ varies with at. no., reaching a max. of 2·3% at Ca (20). N. M. B.

**Variation of the atomic structure factor of potassium with *X*-ray wave-length.** S. K. Allison and W. P. Jesse (Physical Rev., 1936, [ii], **49**, 483—494).—Using a special vac. ionisation spectrometer the diffracted power in the Debye–Scherrer rings from NaCl, NaF, LiF, and KF powders has been compared. For KF, with the range 1·538—4·146 A., the expected decrease of the crystal structure factor on the short-$\lambda$ side was observed; beyond the *K* edge of K the factor rose again, but considerably more than predicted. It is concluded that Höni's computations based on the wave-mechanical theory of *X*-ray dispersion do not correctly give the observed structure factor differences for the (200) diffraction halo from powdered KF on the long and short $\lambda$ sides of the K *K* edge. The predicted invariance of the structure factor decrement due to *K* electrons with scattering angle for light elements is confirmed. N. M. B.

**Auger effect and relative intensity of *L*-emission lines.** D. Coster and K. W. de Langen (Physica, 1936, 3, 282—288).—The relative intensities of the $L\beta_1$, $\beta_3$, and $\beta_4$ lines of Ag, Sn, and Sb have been determined. With Ag, the Auger effect $L_I \rightarrow L_{III}$ with ejection of an *M* electron can take place, and this leads to markedly smaller vals. of the intensity ratios $\beta_3 : \beta_1$ and $\beta_4 : \beta_1$. L. J. J.

**Relativistic theory of the Auger effect.** H. S. W. Massey and E. H. S. Burhop (Proc. Roy. Soc., 1936, A, 153, 661—682).—Calculations have been made of the probability of the internal conversion of the *K* series radiation for Au arising from the interaction of the $L_IL_I$, $L_IL_{II}$, and $L_IL_{III}$ shells, using Møller's method (A., 1932, 980). Less accurate calculations have also been made for Ag. Appreciable relativistic effects have been found for both metals, most marked in the case of Au. L. L. B.

***K X*-Ray absorption spectra of some compounds of bromine and rubidium.** S. T. Stephenson (Physical Rev., 1936, [ii], 49, 495—498).—Using powder absorbing screens with a double-crystal ionisation spectrometer and MeI in the ionisation chamber to eliminate the effect of Br in MeBr, the *K X*-ray absorption spectrum of Br in KBr, RbBr, $CdBr_2$, and $NaBrO_3$ and of Rb in RbBr was obtained. The widths of the Br and Rb edges were about 9 and 11 volts, respectively. No discontinuity due to a possible simultaneous ejection of *K* and *L* electrons was observed. N. M. B.

**Ultra-soft *X*-ray absorption edges from the emulsion and sensitisers of photographic plates.** J. M. Bačkovský and V. Dolejšek (Z. Physik, 1936, 99, 42—51).—The intense absorption of ultra-soft *X*-rays gives inverted absorption edges of K, Cl, and Ca ($L_{II-III}$ edges) as well as those of Ag and Br. A. B. D. C.

**Approximate method for the calculation of the work of emission of electrons from metals.** E. H. B. Bartelink (Physica, 1936, 3, 193—204).—Mathematical. L. J. J.

**Relation between secondary emission and work function.** L. R. G. Treloar (Nature, 1936, 137, 579).—Secondary emission from a Mo filament with different degrees of Ba surface has been investigated. L. S. T.

**Electron emission of the cathode of an arc.** M. J. Druyvesteyn (Nature, 1936, 137, 580).—A new way in which electrons may escape from the cathode of an arc is suggested. L. S. T.

**Production of intense beams of slow electrons.** R. Planiol (Compt. rend., 1936, 202, 1267—1268).—A supplementary grid, at a high positive potential, is interposed between the emitting filament and the principal grid. L. J. J.

**Theoretical cross-section for *K*-electron ionisation by electron impact.** W. W. Wetzel (Physical Rev., 1936, [ii], 49, 531—534).—Mathematical. An expression is found for the cross-section as a function of the at. no., the ionisation potential of the *K* shell, and the energy of the colliding electron. N. M. B.

**Distribution of electron velocities in the magnetic field.** T. V. Ionescu and C. Mihul (Compt. rend., 1936, 202, 1160—1162).—Electrons produced by a heated W filament were accelerated by different voltages (240—1920 volts) between two grids, under the action of a magnetic field (0—43·2 gauss). The resulting ionisation currents in the gas space between the second grid and a plate at different voltages were plotted against the plate voltage. M. S. B.

**Collision of slow electrons in pure oxygen. Electronic affinity.** L. Goldstein (Compt. rend., 1936, 202, 924—926).—Pure dry $O_2$ behaves towards electrons of energy 0·1—5·9 e.v. like rare gases. Electrons of greater energy dissociate $O_2$, but they are not captured by mol. $O_2$. H. J. E.

**Determination of the velocity distribution of electrons in a low-pressure discharge tube.** A. H. van Gorcum (Physica, 1936, 3, 207—218).—A method of applying Druyvesteyn's formula (*A.*, 1930, 1490) is described. The velocity distribution in a Ne tube changes to a Maxwellian one as the positive column is approached from the cathode side. L. J. J.

**Motion of electrons in electric and magnetic fields taking into consideration the action of the space charge.** S. J. Braude (Physikal. Z. Sowiet-union, 1936, 8, 667—674; cf. A., 1935, 1294).—Theoretical. The motion of electrons in crossed electric and magnetic fields with space charge is investigated for a cylindrical condenser. A. J. M.

**Positron theory and proper energies.** R. Serber (Physical Rev., 1936, [ii], 49, 545—550).—Mathematical. N. M. B.

**Production of positrons from bismuth.** H. P. De (Indian J. Physics, 1936, 10, 103—108).—The production of positrons from Bi bombarded with neutrons and other radiations from a mixture of MsTh, Ra, and BeO was examined by the cloud-chamber method, using a stereo-camera. For 282 electron tracks there were 20 positron tracks. The energy of the positrons was $10^5$—$4{\cdot}5 \times 10^6$ e.v. It is suggested that the positron emission is due to internal conversion of high-energy $\gamma$-radiation. A. J. M.

**Sign of the magnetic moment of the proton and of the deuteron.** J. M. B. Kellogg, I. I. Rabi, and J. R. Zacharias (Nature, 1936, 137, 658).—Both moments are positive. L. S. T.

**Production of high-velocity ions for the disintegration of atomic nuclei.** R. J. Moon and W. D. Harkins (Science, 1936, 83, 244). L. S. T.

**Kinetic energy of positive thermions of some halides.** (MLLE.) C. TUDOR (Bull. Acad. Sci. Roumaine, 1935, **17**, 111—115).—Positive ion emission has been studied with the chlorides of Sn, Zn, Sr, Cd, Cu$^{I}$, and Li, $Ba(NO_3)_2$, $SrBr_2$, KBr, $CdI_2$, and $ZnI_2$. The mean kinetic energy of the ions has been determined. R. S. B.

**Ionisation and luminescence of atomic beams in a high vacuum.** R. PLANIOL (Compt. rend., 1936, **202**, 1032—1033; cf. A., 1935, 599).—An improved apparatus is described. The passage of electrons through an at. beam is marked by a luminescence which increases with the intensity of the beam and changes from violet to blue. The light is emitted in the visible and ultra-violet. R. S. B.

**Direct determination of the effective radius of strongly vibrating molecules by the molecular beam method.** N. SASAKI and E. NISHIBORI (Proc. Imp. Acad. Tokyo, 1936, **12**, 10—12).—The mols. are strongly excited photochemically and their effective radius is found by the mol. beam method. For $I_2$ the ratio of the effective radius of the excited mol. to that of the unexcited mol. is 2·56. A. J. M.

**Ionisation of a molecular beam by electron collision and investigation of the ions produced by the mass spectrograph.** N. SASAKI and E. NISHIBORI (Proc. Imp. Acad. Tokyo, 1936, **12**, 13—15).—The investigation of the primary products of a reaction by the mol. beam method is described. The beams of mols. are ionised and then examined by the mass spectrograph. The method can be used to study the ionisation of mols., or, by crossing beams, the products of reactions. A. J. M.

**Sixth Report of the Committee on Atomic Weights of the International Union of Chemistry.** G. P. BAXTER, O. HÖNIGSCHMID, and P. LEBEAU (J. Amer. Chem. Soc., 1936, **58**, 541—548).—Changes have been made in the at. wt. of Ta (180·88) and Ra (226·05). Pa (at. wt. 231) has been added to the table. E. S. H.

**Relative at. wt. of oxygen in water and in air; atmospheric distribution of the oxygen isotopes and the chemical standard of at. wts.** M. DOLE (J. Chem. Physics, 1936, **4**, 268—275).—Density measurements on $H_2O$ made from tank $H_2$ and $O_2$ from the air and from tank $H_2$ and $O_2$ from the $H_2O$ of Lake Michigan are recorded. The former is 6·0±0·6 p.p.m. heavier, corresponding with a difference of 0·000108±0·00001 at. wt. units between the at. wts. of O in air and $H_2O$. The results are discussed in relation to existing data. The possibility of accounting for the observed difference by isotopic exchange and gravitational equilibria in the stratosphere, and its bearing on the basis of at. wt. standards, are considered. L. J. J.

**Eighth isotope of molybdenum.** J. DE GIER and P. ZEEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 327—329).—Using $Mo(CO)_6$+50% $O_2$ in the discharge a new isotope $^{102}$Mo has been detected, in agreement with Sitte's prediction (cf. A., 1935, 1295). The provisional abundance is 2—3%. R. S. B.

**At. wt. of rubidium.** E. H. ARCHIBALD and J. G. HOOLEY (J. Amer. Chem. Soc., 1934, **58**, 618—619).—From determinations of the ratios RbBr : Ag and RbBr : AgBr, the at. wt. of Rb is 85·481. E. S. H.

**At. wt. of germanium. II. Analysis of germanium tetrachloride.** O. HÖNIGSCHMID and K. WINTERSBERGER (Z. anorg. Chem., 1936, **227**, 17—24; cf. this vol., 5).—The mean of nine nephelometric titrations of $GeCl_4$, the prep. of which is described, gives Ge 72·59±0·006, in agreement with the val. previously obtained. F. L. U.

**Existence of $^{5}$Li.** A. K. BREWER (Physical Rev., 1936, [ii], **49**, 635).—The mass spectra for Li ions emitted thermally from an impregnated Pt source show a peak in the mass no. 5 position and evidence favours $^{5}$Li as its origin. The abundance ratio for the new peak was $^{7}$Li/$^{5}$Li=20,000±1000. N. M. B.

**New data on isotopes.** F. W. ASTON (Nature, 1936, **137**, 613; cf. this vol., 400).—Isotopic wts. obtained by the doublet method are $^{10}$B 10·0161±0·0003, $^{14}$N 14·0073±0·0005, $^{19}$F 19·0045±0·0006, $^{20}$Ne 19·9986±0·0006, $^{27}$Al 26·9909, $^{28}$Si 27·9860, $^{29}$Si 28·9864±0·0008, and $^{40}$A 39·9754±0·0014. The corresponding packing fractions are 16·1, 5·28, 2·36, −0·70, −3·3, −5·0, −4·7, and −6·15, respectively. The present position with regard to some doubtful isotopes is reviewed. The existence of $^{58}$Fe and $^{64}$Ni is supported by the work of de Gier and Zeeman (this vol., 5, 130), but evidence as to $^{61}$Ni is still conflicting. If the lines 148 and 150 obtained by Dempster are due to isotopes of Nd, as is probable, the discrepancy between the physical and chemical at. wts. of Nd may disappear. Revised vals. for the percentage abundances of the various isotopes of Cd, Sn, and Pb are given. L. S. T.

**Periodic system of the elements and element 93.** M. CARRANZA (Bol. Soc. Quim. Peru, 1935, **1**, 41—45).—A review. L. A. O'N.

**Radioactivity of samarium.** R. HOSEMANN (Z. Physik, 1936, **99**, 405—427).—The range of α-rays emitted at the rate of 89 per sec. per g. is 1·13 cm. in air at 15° and 760 mm. A. B. D. C.

**Existence of the $\alpha_5$ radiation and the separation of the magnetic spectrum of thorium-*C* into two series.** S. ROSENBLUM (Compt. rend., 1936, **202**, 943—946; cf. A., 1932, 442).—A discussion. The existence of $\alpha_5$ radiation is reaffirmed. Its intensity is low. H. J. E.

**Tracks of the α-particles of thorium and its products.** H. J. TAYLOR and V. D. DABHOLKAR (Proc. Indian Acad. Sci., 1936, **3**, **A**, 265—271).—The tracks of α-particles emitted from atoms of the Th series in a photographic emulsion have been recorded (cf. A., 1935, 910). Single tracks and stars, characteristic of the individual atoms of the various members of the series, are obtained. L. J. J.

**Intensity of fine-structure groups in the α-ray magnetic spectra of radioactinium and its products.** S. ROSENBLUM, M. GUILLOT, and (MLLE.) M. PEREY (Compt. rend., 1936, **202**, 1274—1276).—Data are recorded for the relative intensities of

11 known lines of RdAc and 4 of Ac-*X*. Four new lines are recorded for actinon, and two new lines for Ac-*C*. L. J. J.

**Tracks of swift nuclei in photographic emulsions.** H. J. Taylor (J. Univ. Bombay, 1935, 4, Part II, 70—73; cf. A., 1935, 910).—The photographic method is not so widely applicable as the cloud chamber method, but has greater sensitivity in recording the tracks of $\alpha$-particles, recoil protons, and tracks resulting from nuclear disintegration under neutron bombardment. Investigations can cover all tracks over longer periods, and being recorded in small area enable rare events, *e.g.*, the reaction $^{10}B+{}^{1}n \rightarrow {}^{4}He+{}^{4}He+{}^{3}He$, to be observed. J. W. S.

**Calorimetric measurements of the energy of disintegration in the actinium family.** A. Sanielevici (Compt. rend., 1936, **202**, 1055—1057).—Using an adiabatic micro-calorimeter the following energy ($E$) changes have been measured: for Ac in equilibrium $E$ ($\alpha$+recoil)$=7{\cdot}15\times10^{-3}$ g.-cal. per g. per hr.; for Ac → Ac-$C''$ $E$ ($\alpha$+recoil) represents 90·9, $E$ ($\beta$ primary) 2·4, and $E$ ($\gamma+\beta$ secondary) 6·7% of the whole. The mean $E$ of the $\beta$-rays of Ac-$B$ is $3{\cdot}7\times10^{5}\pm3\%$ e.v. R. S. B.

**Continuous $\beta$ spectrum of actinium-*B*.** M. Lecoin (Compt. rend., 1936, **202**, 1057—1059; cf. A., 1935, 1048).—The $\beta$ spectrum of initially pure Ac-$B$ has been studied. The curve for disintegration no. against energy shows a max. at $5\times10^{5}$ e.v. after allowing for the influence of Ac-$C''$. The mean energy for the $\beta$-radiation of Ac-$B$ is $3{\cdot}6\times10^{5}$ e.v., in agreement with Sanielevici (see above). The higher limit of the spectrum occurs at $9{\cdot}5\times10^{5}$ e.v. R. S. B.

**Radiation from the active deposit of actinium.** J. Surugue (Compt. rend., 1936, **202**, 410—411; cf. A., 1933, 659).—The energies of the $\beta$-rays from the active deposit of Ac, as compared with the $F$ ray of Th-$B$, are found to be 0·4% > previously recorded. A new ray of high energy (813 e.kv.) is found and attributed to the transformation Ac-$B$ → Ac-$C$. The change Ac → Ac-$C''$ yields only the $\beta$-ray of 350 e.kv., in accord with the fine structure of the $\alpha$-radiation. J. W. S.

**Continuous $\beta$-ray spectrum of radium-$C''$.** L. Goldstein and M. Lecoin (Compt. rend., 1936, **202**, 1169—1170).—The $\beta$-ray spectrum of Ra-$C''$ has been photographed using a Wilson expansion chamber. Under the experimental conditions positrons were distinguished from electrons and thus possible interferences from the disintegration of the synthetic element $R_9F$, produced by the bombardment of N by the $\alpha$-rays of Ra-$C'$, could be eliminated. It is shown that at least two energy quanta, equal to a total of $3{\cdot}4\times10^{6}$ e.v., are emitted in the disintegration of Ra-$C''$. M. S. B.

**Slow neutrons.** E. Fermi and F. Rasetti (Nuovo Cim., 1935, [ii], 12, 201—210; Chem. Zentr., 1935, ii, 1127).—Data are given for the absorption coeffs. of B and Cd for neutrons slowed by elastic collision with H atoms. The absorption mechanism may differ as an unstable radioactive isotope or a stable isotope is formed by neutron capture. J. S. A.

**Absorption of slow neutrons.** C. H. Collie (Nature, 1936, **137**, 614).—The absorption of slow neutrons from a Rn–Be source by several elements has been measured using an improved arrangement. The absorption band of Cd occurs in the range 0—1·5 e.v. and a very narrow absorption band (0—0·1 e.v.) is indicated. The band for In occurs in the same range and partly overlaps that of Cd. No effect due to the sp. absorption of Au or Ag could be found. L. S. T.

**Capture of slow neutrons.** G. Breit and E. Wigner (Physical Rev., 1936, [ii], 49, 519—531).—Mathematical. Considerations are given to account for the contradiction of current theories of the large cross-section of slow neutrons by frequent absence of strong scattering in good absorbers and existence of resonance bands. N. M. B.

**Retardation of neutrons by collision with protons.** E. Lamla (Naturwiss., 1936, 24, 251—252).—Theoretical. The energy distribution of neutrons after collision with protons is calc., both particles being treated as elastic spheres. A. J. M.

**Diffraction of slow neutrons by crystalline substances.** W. M. Elsasser (Compt. rend., 1936, **202**, 1029—1030).—Theoretical. Crit. angles of 26° have been calc. for Ni and Fe, and 25° for Cu. R. S. B.

**Disintegration of boron.** D. Roaf (Proc. Roy. Soc., 1936, **A**, **153**, 568—576).—Using $BF_3$ in a Wilson chamber, the recoils from the disintegration of $^{10}_{5}B$ by neutrons have been photographed and their energy has been measured. Most of the disintegrations were caused by neutrons of $< 2\times10^{4}$ e.v., but one was observed due to a neutron of energy $> 10^{5}$ e.v. The energy released in the reaction $^{10}_{5}B+{}^{1}_{0}n={}^{7}_{3}Li+{}^{4}_{2}He$ is $1{\cdot}50\pm0{\cdot}05\times10^{-3}$ units of at. mass. The $^{10}_{5}B$ mass has been corr. to $10{\cdot}0136\pm0{\cdot}0014$. L. L. B.

**Radioactivity and atomic theory.** (Lord) Rutherford (J.C.S., 1936, 508—516).—Faraday lecture.

**Deviation in passing through magnetised iron of (I) high-energy charged particles, (II) cosmic-ray charged particles.** (I) W. F. G. Swann, (II) W. E. Danforth, and W. F. G. Swann (Physical Rev., 1936, [ii], 49, 574—582, 582—591).—I. Mathematical.

II. Investigations by means of Geiger counters of the deflexions of cosmic-ray electrons in passing through the saturated Fe core of an electromagnet are described. Observed effects are compared with calc. results to determine limits of the effective magnetic vector within the Fe. N. M. B.

**Geomagnetic effect on cosmic radiation in the stratosphere.** M. G. E. Cosyns (Nature, 1936, **137**, 616). L. S. T.

**Structure of cosmic rays.** R. Hilgert and W. Bothe (Z. Physik, 1936, 99, 353—362). A. B. D. C.

**Nature and range of radiation particles (collision radiation) involved in Hoffmann collisions.** H. Nie (Z. Physik, 1936, 99, 453—480).—The effect of various thicknesses of Pb, Fe, and Al shields is described. A. B. D. C.

**Relationship between Hoffmann collisions and showers.** J. Bøggild (Naturwiss., 1936, **24**, 280—281). A. J. M.

**Rôle of chemistry in the study of atomic transmutation.** F. A. Paneth (Nature, 1936, **137**, 560—562).—A review. L. S. T.

**Artificially radioactive materials.** E. Segrè (Nuovo Cim., 1935, [ii], **12**, 232—239; Chem. Zentr., 1935, ii, 1129).—The life periods of a no. of artificial radio-elements are correlated with the hardness of the emitted β-radiation, as measured by absorption in Al. The variation in intensity of different activities of the same element on activation with fast and slow neutrons (*e.g.*, comparison of the behaviour of the 20-min. and 23-hr. periods of Ga) is discussed. J. S. A.

**Nuclear processes with the mean corpuscular energy of star centres.** R. Döpel (Naturwiss., 1936, **24**, 237).—The nuclear reactions ${}^2_1D+{}^2_1D={}^3_1H+{}^1_1H$ and ${}^2_1D+{}^2_1D={}^3_2He+{}^1_0n$ have been observed at potentials < previously. The efficiency of the first reaction was $10^{-16}$ at 5 kv., and $10^{-14}$ at 15 kv. The efficiency of the second reaction was somewhat greater. 5000 e.kv. corresponds with the mean energy of the atoms in the centre of a star at a temp. of $4\times10^{7\circ}$. Hence transmutation occurring in stars can now be investigated in the laboratory under similar conditions. A. J. M.

**Radioactive elements of low atomic number.** W. A. Fowler, L. A. Delsasso, and C. C. Lauritsen (Physical Rev., 1936, [ii], **49**, 561—574).—Radioactive elements of low at. no. were produced by bombarding Li, B, C, $NaNO_2$, and CaF with high-velocity deuterons. The energy distribution of the electrons and positrons emitted was determined by a Wilson cloud-chamber and magnetic field. The electron and positron spectra max. energy ranges are 5—13 and 1—2 m.e.v., respectively. The form of the spectra agrees with the Konopinski theory (cf. A., 1935, 1048). Data are tabulated for the radioactive elements ${}^9_5B$, ${}^{11}_6C$, ${}^{13}_7N$, ${}^{15}_8O$, ${}^{17}_9F$, ${}^8_3Li$, ${}^{12}_5B$, ${}^{16}_7N$, and ${}^{20}_9F$. N. M. B.

**Radioactive argon.** A. H. Snell (Physical Rev., 1936, [ii], **49**, 555—560).—When bombarded with high-speed deuterons, A yields a radioactive product with decay period 110±1 min., and emitting negative electrons. The activity is shown chemically to be due to an A isotope, and the reaction is probably ${}^{40}A+{}^2H={}^{41}A+{}^1H$. Absorption measurements of the β-particles show a max. energy of about 1·1 mv. (cf. Kurie, this vol., 542). The excitation function of the radioactivity favours the Oppenheimer–Phillips (cf. A., 1935, 1296) rather than the Gamow theory for this type of reaction. The same radioactive substance was made by intense bombardment of A by neutrons. N. M. B.

**Time decay of atomic nuclear processes.** R. Döpel (Z. Physik, 1936, **99**, 161—168).—Time decay of α-ray artificial radioactivity was detected for In, Cs, and Ce. A. B. D. C.

**Artificial radioactivity of tin.** M. E. Nahmias (Compt. rend., 1936, **202**, 1050—1052).—Sn shows a feeble induced radioactivity after irradiation by neutrons from Rn–Be in air and paraffin. Chemically pure and commercial Sn give the same result, probably due to the reaction ${}^{122}_{50}Sn+{}^1_0n \rightarrow {}^{123}_{50}Sn \rightarrow {}^{123}_{51}Sb+e^-$, the small % of the isotope 122 (5%) accounting for the feebleness of the induced radioactivity. The period is 5·3—7·1 min. R. S. B.

**Induced radioactivity of nickel and tin.** R. Naidu (Nature, 1936, **137**, 578—579).—When irradiated by slow neutrons from a Rn–Be source, Geiger–Müller counters with walls of Ni and Sn show induced radioactivity. With Ni the half-life period is 180±10 min. and with Sn, 8±2 and 18±2 min. L. S. T.

**Artificial radioactivity produced by bombardment with neutrons. VII—IX.** E. Amaldi, O. D'Agostino, E. Fermi, B. Pontecorvo, F. Rasetti, and E. Segrè (Ric. sci. Prog. tec., 1934, 5, II, 467—470; 1935, 6, I, 123—125, 435—437; Chem. Zentr., 1935, ii, 969—970).—VII. New activities and their respective half-life periods are recorded for K, Ga, Cd, In, Sb, Pr, Mn, As, and Rh. Separation of the active material by Szilard and Chalmers' method (A., 1934, 1152) has been applied to Cl, As, and Mn in org. and inorg. compounds. Effective collision areas for Cl, Co, Ag, Cd, In, I, Pr, Au, and Hg are recorded. Increase in the efficiency of activation by surrounding the neutron source with Pb, graphite, and basalt in place of H compounds is discussed.

VIII. Half-val. periods are recorded for Mg, Si, Ba, Gd and W (new activities), and for Si, P, V, Ga, Br, Ag, I, Pr, Re, Ir, and Au (more accurate data). γ-Ray activity has been detected with Rh, Br, V, Mn, Cu, Ga, In, Sb, I, W. For B, the nuclear reaction ${}^{10}_5B+{}^1_0n={}^7_3Li+{}^4_2He$ is advanced. Chemical separation of the active species produced from Sb, W, and Re show them to be isotopes of these elements.

IX. Accurate life periods are recorded for Al, S, Cl, Cu, Zn, Ga, Rh, Sb, and Th. Chemical separation of the active material from P, Cl, Cu, Ga, and Si shows the activity to belong to an isotope of the same element; the activity of Zn is due to a Cu isotope. The 10-sec., 13-min., and 100-min. activities of neutron-activated U are attributed to sucessive transformations, probably of the elements 92, 93, and 94, all of at. wt. 239. Co, Cu, and Au emit γ-rays. J. S. A.

**Artificial radioactivity induced by neutron bombardment.** I. V. Kurtschatov, G. D. Latischev, L. M. Nemenov, and I. P. Selinov (Physikal. Z. Sovietunion, 1936, **8**, 589—594; cf. A., 1935, 1050).—The radioactivity produced in Pd, Re, and Os when bombarded with slow neutrons was investigated. In the case of Pd, the existence of two active substances of half-life 15 min. and 12 hr., respectively (Fermi, A., 1934, 1284), has been confirmed, and two further substances of half-life 3 min. and approx. 60 hr., respectively, have been found. With Re, two radioactive substances of half-life 20 and 85 hr., respectively, have been obtained. Os gives only a very weak activity of half-life approx. 40 hr. A. J. M.

**Intensity of scattered radiation from moving free electrons.** E. C. G. Stueckelberg (Helv. phys. Acta, 1935, **8**, 197—204; Chem. Zentr., 1935, ii, 986).—Theoretical. J. S. A.

**Electronic nature of light.** J. L. Destouches (Compt. rend., 1936, **202**, 921—923).—Theoretical. H. J. E.

**Concept of [chemical] element.** (Mlle.) C. Ramnoux and J. Martinet (Bull. Soc. chim., 1935, [v], **2**, 1474—1485).—The present meaning of the word "element" is not sufficiently precise. Considerable restriction in its use is suggested, to avoid confusion and ambiguities. R. C. M.

**Properties of the spin of a system of corpuscles.** J. L. Destouches (Compt. rend., 1936, **202**, 387—389).—Mathematical. J. W. S.

**Deviations from the Maxwell equations resulting from the theory of the positron.** N. Kemmer and V. Weisskopf (Nature, 1936, **137**, 659). L. S. T.

**Structure of atomic nuclei.** H. A. Wilson (Proc. Roy. Soc., 1936, **A**, **153**, 493—504; cf. this vol., 266).—The energies of formation of several atoms have been calc. from nuclear reaction energies. Assuming that the energy is due to the formation of linkings between the neutrons and protons forming the atom, arrangements of neutrons and protons and linking energies are found which give the correct vals. of energies of formation. L. L. B.

**Origin of mass in neutrons and protons.** M. N. Saha (Indian J. Physics, 1936, **10**, 141—153).—Theoretical. A. J. M.

**Neutron-proton exchange interaction.** M. S. Plesset (Physical Rev., 1936, [ii], **49**, 551; cf. Breit, this vol., 134).—Mathematical. N. M. B.

**Conservation of energy and momentum in atomic processes.** E. J. Williams (Nature, 1936, **137**, 614—615).—The uncertainty principle is discussed in connexion with Shankland's results (this vol., 265). L. S. T.

**Exchange rules in the neutrino theory of light.** P. Jordan (Z. Physik, 1936, **99**, 109—113). A. B. D. C.

**Heisenberg's oscillator model and nuclear moments.** P. Pavinski (Compt. rend. Acad. Sci. U.R.S.S., 1936, **1**, 169—171).—Using a simplified Hartree method with the "eigen"-functions of the spatial harmonic oscillator to describe the states of the individual particles, in conjunction with the Lande assumption that only the unpaired proton is responsible for the mechanical and magnetic moments of a nucleus, it is possible to calculate these moments, in agreement with experiment. A. J. M.

**Theory of the relativistic degenerate corpuscular gases and their employment in the atomistic theory of Brownian molecular motion.** M. Satô (Sci. Rep. Tôhoku, 1936, **24**, 565—586).—On the basis of Glaser's theory (A., 1935, 679) the dynamics of the pressure of light and the atomistic theory of Brownian movement have been studied. Earlier work (A., 1934, 252) is discussed. M. S. B.

**Oil-drop method and the electronic charge.** E. Bäcklin and H. Flemberg (Nature, 1936, **137**, 655—656).—Preliminary results with an improved apparatus give $e = 4{\cdot}800 \times 10^{-10}$ abs. e.s.u. in good agreement with spectroscopic vals. L. S. T.

**Measurement of *e*/*m* with a triode valve.** S. Ram (Indian J. Physics, 1936, **10**, 127—132).—The val. of *e*/*m* has been found by observing the effect of a magnetic field on the grid current of a triode. Two formulæ gave mean vals. for *e*/*m* of $1{\cdot}77 \times 10^7$ and $1{\cdot}79 \times 10^7$, respectively. A. J. M.

**Relation between the fundamental constants of physics.** A. Haas (Physical Rev., 1936, [ii], **49**, 636).—Mathematical. N. M. B.

**New electrodynamics and the fine structure constant.** L. Infeld (Nature, 1936, **137**, 658). L. S. T.

**Determination of the constant α of fine structure by the unitary theory of the electromagnetic field.** S. A. de Mayolo (Bol. Soc. Quim. Peru, 1935, **1**, 26—40).—The unitary theory, by which the electromagnetic field in a vac. is due to central forces exerted between two equal non-corpuscular quantities of electricity, of opposite sign, in dynamic equilibrium, moving with the velocity of light, is further developed. L. A. O'N.

**Absorption spectra of iodine solutions. I. Solutions in mineral acids.** A. V. Pamfilov and R. V. Teis (J. Gen. Chem. Russ., 1935, **5**, 1833—1838).—The absorption spectra of I in aq. HCl or $H_2SO_4$ are of the same type as in org. solvents. R. T.

**Ultra-violet absorption of ice.** E. J. Cassel (Proc. Roy. Soc., 1936, **A**, **153**, 534—541).—The thin films of ice used showed a continuous absorption with a long-λ limit at about 1670 A., which varied only slowly with the thickness of the film, indicating an abrupt rise in the coeff. of absorption. The absorption band of ice is shifted towards short waves relatively to that of vapour by 0·6—0·7 e.v. The absorption of heavy ice begins at a shorter λ than that of light ice, and the amount of the shift is of the same order of magnitude as that found for $H_2O$ vapour by Franck and Wood (A., 1934, 828). L. L. B.

**New bands of nitric oxide.** M. Duffieux and L. Grillet (Compt. rend., 1936, **202**, 937—939; cf. A., 1935, 1051).—Measurements of rotational fine structure are recorded for the bands about 6000 A. previously described, which are attributed to ionised NO. H. J. E.

**Absorption spectra of (A) the hydrogen chloride molecule, (B) the hydrogen bromide molecule, and their upper unstable states.** H. Trivedi (Proc. Nat. Acad. Sci. India, 1936, **6**, 18—28, 29—34).—(A) The absorption coeffs. at temp. in the range 20—980° were obtained photographically in an investigation of the continuous absorption spectrum of HCl, and the contributions of individual vibrational levels to the total absorption were found. The vals. of the mol. consts. for the unstable state calc. from observational data at different sets of λλ are in good agreement. The energy of dissociation of the mol. in its unstable state corresponds with the heat of formation of the mol. determined thermochemically.

(B) Investigations and results for HBr are reported similarly to the case of HCl. Analogous agreements are obtained. N. M. B.

**Absorption spectra of hydrochloric acid and various chlorides in the far ultra-violet.** R. Tréhin (Ann. Physique, 1936, [xi], 5, 445—607; cf. A., 1935, 9, 805; 1934, 581; 1933, 111, 1226; 1932, 107; 1931, 19).—Results are given for investigations of the effect of temp. and concn. on the absorption of HCl liquefied, aq., and in $Et_2O$, in the range 2816—1990 A., and of the alkali and alkaline-earth chlorides in aq. solution, of NaCl in glycerol, and of rock-salt, in the range 2500—2170 A. For the aq. solutions the absorption increases as λλ decrease, the effect being more marked with rise of temp. and concn. For each λ and temp. the extinction coeff. increases with concn.; the mol. extinction coeff. increases considerably for low concns. For a given λ and concn. the absorption increases with rise of temp., particularly at higher temp. and shorter λλ, and more rapidly for the acid than for the salts, and as the cation is less hydrated. Results are discussed in relation to the theory of strong electrolytes.
N. M. B.

**Rotation-vibration spectrum of ammonia.** N. Verleger (Naturwiss., 1936, 24, 237).—A new region of strong absorption has been found, extending from 11,600 to 12,400 A. It has the same origin as the 10,230 A. band recently observed and both probably consist of two separate bands, the stronger being that lying farther in the infra-red. A weaker absorption band has been observed at 12,660 A. and consists of a series of strong lines between which is a definite fine structure. A similar weak absorption follows the 10,230 A. strong band, at 10,900 A.
A. J. M.

**Band spectra of PH and NH.** C. Gilbert (Physical Rev., 1936, [ii], 49, 619—624).—Formulæ for the effect of mol. rotation on spin multiplets are considered for triplet cases, and mol. consts. are calc. Results are compared with experimental data for the λ 3400 band of PH and the λ 3360 band of NH.
N. M. B.

**Spectrum of SiF.** R. K. Asundi and R. Samuel (Current Sci., 1936, 4, 649).—A preliminary announcement of a revised vibrational analysis of the α- and β-bands, and an analysis of the γ-bands. The consts. of the mol. in its various electronic states are given.
N. M. B.

**Isotope displacements in the band spectrum of mercury deuteride.** S. Mrozowski (Z. Physik, 1936, 99, 236—251). A. B. D. C.

**Ultra-violet bands of beryllium oxide.** A. Ciccone (Ric. sci. Prog. tec., 1935, 6, 123; Chem. Zentr., 1935, ii, 976).—The BeO bands from a vac. arc between Be electrodes in $O_2$ are recorded.

**Absorption spectrum of lead oxide (PbO).** H. G. Howell (Proc. Roy. Soc., 1936, **A**, 153, 683—698).—The spectrum stretches from 2600 to 6000 A. and contains 5 systems, 3 of which are found in emission. The vibrational consts. of all the levels involved have been determined. The ground state probably dissociates into 2 excited atoms. The spectra of the related mols. PbS, PbO, SnS, SnO, GeS, and GeO are compared; among other similarities, it is found that the vibrational frequency varies from state to state in a similar manner with oxide and sulphide mols.
L. L. B.

**Absorption spectra of nitrates in the vapour state.** M. I. Haq and R. Samuel (Nature, 1936, 137, 496).—The absorption spectra of K, Ag, Mg, and Pb nitrates, obtained by heating the salt in a vac. to approx. 100° > m.p., show a flat and diffuse max. of selective absorption between 270 and 260 mμ, indicating that the nitrates are covalently bound in the vapour state. Some nitrites and sulphates show a similar phenomenon.
L. S. T.

**Carbon monoxide bands $A^1\Pi \rightarrow X^1\Sigma$ (IV Pos.).** L. Gerö (Z. Physik, 1936, 99, 52—64).—Rotation analysis is given between 1950 and 2700 A.
A. B. D. C.

**Predissociation in the $A^1\Pi$ level of CO; dissociation energy of carbon monoxide at 6·9 volts?** R. Schmid and L. Gerö (Z. Physik, 1936, 99, 281—284).—The predissociation limits at 9·57, 11·06, and 11·54 volts are best co-ordinated by the assumption of a ground level dissociation energy of 6·9 volts. The reaction $C_{solid} \rightarrow C\ (^5S)$ is given as 177 kg.-cal.
A. B. D. C.

**Transmission of visible light through artificial homogeneous clouds.** G. R. Paranjpe and N. N. Bhagvat (J. Univ. Bombay, 1935, 4, Part II, 28—64).—The transmission of light through clouds of $H_2O$, $CHCl_3$, and $CCl_4$ agrees fairly well with Stratton and Houghton's theory (Physical Rev., 1931, [ii], 38, 159). With kerosene only partial agreement is obtained, and with EtOH, PhMe, and $NH_2Ph$ no agreement. No conclusions can be reached relating the effect with the refractive index of the liquid. For all liquids except EtOH and $NH_2Ph$ red light is transmitted better than blue by large drops, contrary to theory. J. W. S.

**Ultra-violet spectra of bromine derivatives of aniline.** (Mme.) M. P. Rumpf and P. Rumpf (Compt. rend., 1936, 202, 1063—1065).—The absorption of $NH_2Ph$ and its $Br_1$-, $Br_2$-, $Br_3$-, and $Br_5$-derivatives, *p*-$C_6H_4Cl{\cdot}NH_2$, 4-chloro- and 4-nitro-2 : 6-dibromoaniline have been determined in EtOH and $C_6H_{14}$. There is only one band in EtOH in contrast to the many bands in $C_6H_{14}$. Replacement of H by Br displaces the absorption max. towards the higher λ, the displacement increasing in the order *m*, *o*, and *p*, with the exception of *o*- and *m*-$C_6H_4Br{\cdot}NH_2$, for which the max. occur in the same position. Cl has the same influence as Br, but $NO_2$ is more effective in displacing the bands. On acetylation of the *p*-$Br_1$- and the 2 : 4 : 6-$Br_3$-derivatives the bands disappear, but in alcoholic NaOH intense absorption occurs. The $Br_1$- and $Br_3$-derivatives in aq. EtOH containing HCl give no bands, except for 2 : 6-$C_6H_3Br_2{\cdot}NH_2$, which is a very weak base. R. S. B.

**Influence of cyclisation on the "colour" of molecules. Ultra-violet absorption of derivatives of diphenylurethane and fluorene.**—See this vol., 726.

**Absorption spectra. I. Application to intermediate products of dyes.** (Mlle.) C. L. Harberts, P. M. Heertjes, L. J. N. van der Hulst, and

H. I. WATERMAN (Bull. Soc. chim., 1936, [v], **3**, 643—655).—The absorption spectra of $NH_2Ph$, $NH_2Ph,HCl$, $PhN_2Cl$, *p*-toluidine, *p*-$C_6H_4Me\cdot N_2Cl$, and $(NPh\colon)_2$ in $H_2O$, EtOH, or hexane have been determined.
E. S. H.

**Spectrochemistry of organic nitrogen compounds.** (MME.) RAMART-LUCAS (Bull. Soc. chim., 1936, [v], **3**, 723—738).—A preliminary discussion.
E. S. H.

**Absorption and deformation of valency angles.** (MME.) RAMART-LUCAS (Bull. Soc. chim., 1936, [v], **3**, 738—745).—A preliminary discussion of work to be published on the absorption spectra of org. compounds. E. S. H.

**State of the benzene molecule in solution.**—See this vol., 713.

**Absorption spectrum of dinaphthopyrone.** W. SATURNINA (Acta phys. polon., 1933, **2**, 283—284; Chem. Zentr., 1935, ii, 1159).—Three max. (3540, 3375, and 3175 A.) are shown. H. N. R.

**Optical absorption of porphyrins. V.** A. STERN and H. WENDERLEIN (Z. physikal. Chem., 1936, **176**, 81—124; cf. this vol., 545).—In normal porphyrins with an oximated CO group the $\colon N\cdot OH$ group has little effect on the optical absorption, whereas with porphyrins having one CO group only, and that in the isocyclic ring, the effect of the $\colon N\cdot OH$ is greater, the absorption curve being of the rhodo-type. In general, the effect of the $\colon N\cdot OH$ is in the direction of a curve of the rhodo-type. Porphyrins with a $\cdot CN$ directly attached to one of the nuclei of the porphin framework have a curve of a pronounced rhodo-type. Various substitutions in the dihydroporphin system have a particularly marked effect on the mol. extinction coeff., $\varepsilon$, of the red band I; the influence on the other bands is relatively slight. A $\cdot CHO$ in position 3 or, to a much smaller extent, a $\colon N\cdot OH$ depresses $\varepsilon$. Introduction of Mg raises $\varepsilon$ considerably, and shifts the band max. $\beta\delta$-Di-iminocoproporphyrin II $Me_4$ ester (this vol., 86) appears to be a coproporphyrin II $Me_4$ ester in which only the $\beta$- and $\delta$-C atoms are replaced by *tert.* N. The $\cdot CO_2Me$ in the position 6 in the chlorins has little effect on the optical absorption. A $C\cdot OH$ or similar group with a free CO group at the $\gamma$-C of the porphin system changes the type of the spectrum. The "green anhydride" of Fischer *et al.* (A., 1931, 431) appears to be an anhydride of rhodoporphyrin-XV-$\gamma$-carboxylic acid. The phyllochlorin obtained by heating phylloporphyrin with NaOEt (A., 1929, 941) differs from natural dihydrophyllochlorin only in being optically inactive. R. C.

**Ultra-violet spectrum of hæmoglobin derivatives and bile pigment.** G. A. ADAMS (Nature, 1936, **137**, 578).—Many derivatives of hæmoglobin (enumerated) show an absorption band in the region of 4100 A., due to the porphyrin ring system in the hæm radical, and independent of the nature of the globin present. With bilirubin there is no characteristic band at 4100 A., but a somewhat indefinite absorption from 5000 to approx. 4300 A. L. S. T.

**Ultra-violet absorption of Cellophane and of tissues and vegetable organs.** E. GILLES (Compt. rend., 1936, **202**, 968—970).—The transmission of Cellophane is variable. Absorption becomes considerable at approx. 2200—2600 A. Vegetable membrane transmits light down to 2397 A. Absorption by leaves is intense. Data for various species are given.
H. J. E.

**Infra-red reflexion spectra of silicates. II.** F. MATOSSI and H. KRÜGER (Z. Physik, 1936, **99**, 1—23).—Spectra are given between 8 and 26 $\mu$ for 26 silicates: willemite, zircon, fayalite, olivine, sillimanite, chondrodite, thortveitite, hemimorphite, benitoite, cordierite, ænigmatite, anthophyllite, serpentine, antigorite, agalmatholite, nepheline, cancrinite, scapolite, sodalite, natrolite, danburite, datolite, axinite, epidote, zoisite, and leucite. The spectra fit the scheme already proposed (cf. A., 1934, 829). $Be_2SiO_4$ and $Li_2WO_4$ spectra are compared.
A. B. D. C.

**Infra-red absorption of organic compounds containing hydroxyl and imino-groups.**—See this vol., 718.

**Near infra-red bands of methane. I. General survey, and a new band at 11,050 A.** W. H. J. CHILDS (Proc. Roy. Soc., 1936, **A**, **153**, 555—567).—The near infra-red bands of $CH_4$ in the region 10,000—12,000 A. have been photographed under high dispersion. Much new detail has been observed in the bands at 11,350, 11,620, and 11,870 A., and two new bands have been discovered at 11,050 and 11,230 A. The latter is interpreted as the second harmonic of the fundamental at 3·3 $\mu$, and is described in detail. Several inaccuracies in the consts. of the $CH_4$ mol. derived from Cooley's measurements (A., 1926, 659) are indicated. $I$ in the ground state$=5{\cdot}267\times10^{-40}$ g.cm.$^2$, and the vibration moments of momentum in the 7·7 and 3·3 $\mu$ bands are 0·45 and 0·050, respectively.
L. L. B.

**Rotation-vibration spectrum of acetylene in the photographic infra-red.** G. W. FUNKE (Z. Physik, 1936, **99**, 341—352).—Nine new bands are recorded in this region. A. B. D. C.

**Near infra-red absorption of hydrocarbons. II. Gaseous paraffins, olefines, and acetylene.** P. GÄNSWEIN and R. MECKE. **III. Halogen derivatives of methane, ethane, and ethylene.** O. VIERLING and R. MECKE. **IV. Anharmonic valency vibrations of polyatomic molecules.** R. MECKE (Z. Physik, 1936, **99**, 189—203, 204—216, 217—255).—II. Absorption is given between 10,000 and 7000 A. for $C_2H_6$, $C_3H_8$, $C_4H_{10}$, $C_5H_{12}$, $C_6H_{14}$, $C_2H_4$, $C_3H_6$, $C_4H_8$, $C_4H_6$, $C_2H_2$, $C_4H_2$, $C_4H_4$, and MeCHO. Different degrees of saturation give different absorption regions for the third CH overtone: paraffins absorb between 8950 and 9150 A., olefines between 8600 and 8750 A., and acetylenes from 7850 to 7900 A. (cf. A., 1935, 1444).

III. The third CH overtone was examined for the 6 Cl- and Br-derivatives of $CH_4$, for 5 Cl- and 3 Br-derivatives of $C_2H_6$, for 3 Cl-derivatives of $C_2H_4$, and for $C_3H_7Cl$ and $C_3H_5Cl$. The change in CH bands with halogen substitution is small compared with saturation of the $C\cdot C$ valency, except for unsymmetrical compounds (as $C_2H_3Cl_3$) where bands are ascribed to larger groups (as $CHCl_2\cdot$).

IV. Anharmonic vibration levels are investigated with Schrödinger's vibration equation taking into account perturbations of the second order. Various degrees of coupling and resonance are discussed, particularly in relation to ascribing frequencies to at. groups. The CH group has loose coupling, and its overtones can be described in terms of the fundamental frequency in the ordinary manner.

A. B. D. C.

**Residual ray bands of LiF and MgO.** K. Korth (Nachr. Ges. Wiss. Göttingen, 1935, [ii], **1**, 187—194; Chem. Zentr., 1935, ii, 976).—The proper frequencies of mols. on the surface of LiF and MgO crystals differ from those of mols. in the interior. The reflexion max. $\beta$ and transmission min. $\delta$ are due to interior mols.; the reflexion max. $\alpha$ and transmission min. $\gamma$ are due to surface mols. J. S. A.

**Isolation of the 4358 A. triplet of the mercury arc for use in Raman spectra.** C. Sannié, L. Amy, and V. Poremski (Compt. rend., 1936, **202**, 1042—1044).—The ratio between the densities of the lines 4358 and 4046 A. transmitted by $PhNO_2$ is 60; the ratios for 4358 and 4916 A. transmitted by gentian-violet, rhodamine-S and -5G extra are 10·8, 15·2, and 19. A filter for removing lines of the Hg arc other than 4358 A. in the neighbourhood of this line consists of 6% $PhNO_2$ and 0·01% rhodamine-5G extra in EtOH, the transmission being 1/1000 for 4046 and 4916 A., and 0·95 for 4358 A. The filter changes slowly under the influence of light.

R. S. B.

**Polarisation of the Raman bands of water and deuterium oxide.** R. Ananthakrishnan (Proc. Indian Acad. Sci., 1936, **3**, A, 201—205).—In the three principal Raman bands of $H_2O$ and $D_2O$ the depolarisation increases with frequency shift. The bands 1235 and 175 cm.$^{-1}$ of $D_2O$ are 50—60% and 6/7 depolarised, respectively. The bands 175, 500, and 750 cm.$^{-1}$ of $H_2O$ are highly depolarised. The results are discussed. L. J. J.

**Chlorotitanic acid. Raman spectrum.** (Mme.) M. E. P. Rumpf (Compt. rend., 1936, **202**, 950—952).—Mixtures of $TiCl_4$ and HCl show new Raman lines at 251·7, 340, and 463 cm.$^{-1}$ which, by analogy with corresponding lines for $H_2SnCl_6$, are attributed to $H_2TiCl_6$. The new lines are not observed in a dil. HCl solution of $TiCl_4$. H. J. E.

**Raman spectrum of acetylene.** S. Bhagavantam and A. V. Rao (J. Chem. Physics, 1936, **4**, 293).—The frequencies given by $C_2H_2$ gas are 589, 646, 1973, and 3371 cm.$^{-1}$ Glockler and Morrell's assumption of a bent mol. (this vol., 269) is unnecessary.

L. J. J.

**Raman spectra of deuterochloroform and deuteromethyl alcohol. Vibration model of the type $XY_3Z$.** O. Redlich and F. Pordes (Monatsh., 1936, **67**, 203—212).—The prep. of $CDCl_3$ (from $CCl_3{\cdot}CHO$ and KOD) and MeOD [from $Mg(OMe)_2$ and $D_2O$] is described. Their Raman spectra confirm previously found relations between the frequencies of isotopes. The relations between frequency and force consts. are deduced for the $XY_3Z$-type mol. and the consts. of a central and valency-energy model deduced. The data for $CDCl_3$ can be interpreted either on a central energy model or on a central and valency energy model. J. W. S.

**Raman spectra and vibrations of monodeuterobenzene and *p*-dideuterobenzene.** O. Redlich and W. Stricks (Monatsh., 1936, **67**, 213—221; cf. this vol., 137).—Data recorded previously are expanded and discussed. J. W. S.

**Interpretation of the Raman spectra of formic acid and metallic formates.** J. Gupta (Indian J. Physics, 1936, **10**, 117—125).—The Raman spectra of $HCO_2H$ (liquid and aq. solution), Na, Ba, and Cd formates (solid and aq. solution), and an aq. solution of $CCl_3{\cdot}CO_2Na$ have been investigated. The line 2963 cm.$^{-1}$ observed in the case of pure $HCO_2H$ is also present in the aq. solution of the acid, but in the solid formates it is split into two lines, 2963 and 2574 cm.$^{-1}$; the former is absent from the Raman spectra of solutions of the salts, its place being taken by a line at 2834 cm.$^{-1}$ The 1398 cm.$^{-1}$ line in the spectrum of $HCO_2H$ is also replaced by two (1353, 1375 cm.$^{-1}$) in aq. solutions of the salts, and the two lines at 1675 and 1724 cm.$^{-1}$ for the acid are replaced by one at 1650 cm.$^{-1}$ in solutions of the salts. The shift of the 1398 line to 1353 cm.$^{-1}$ cannot be explained as due to the deformation vibration of CH in the ·CHO (Venkateswaran, this vol., 268), which is responsible for the 1375 line. It is assumed to be due to the oscillation of the $O{\cdot}\ddot{C}{\cdot}O$ group in the Hantzsch structure of formates. A. J. M.

**Constitution of formic acid and formates.** P. B. Sarkar and B. C. Ray (Nature, 1936, **137**, 495—469; cf. A., 1934, 586).—Raman spectra of solutions of $HCO_2H$ and formates, and the infra-red absorption curves of $HCO_2Na$, solid and in aq. solution, indicate that $HCO_2H$ and solid formates are normal in structure for they show the ·CH· linking. Prototropic change of the true formate ion, H·C(O)·H into C(O)·OH is suggested to account for this. L. S. T.

**Constitution of formic acid and formates.** I. T. S. Wheeler. II. T. R. Seshadri. III. R. M. Halasyam (Current Sci., 1936, **4**, 650—651).—I. The parachor vals. for $HCO_2H$ are discussed (cf. Halasyam, this vol., 412).

II, III. Polemical. N. M. B.

**Raman and infra-red spectra of stereoisomeric 1 : 3- and 1 : 4-dimethyl*cyclo*hexanes and of 1 : 1-dimethyl*cyclo*hexane.** J. Lecomte, L. Piaux, and O. Miller (Bull. Soc. chim. Belg., 1936, **45**, 123—129).—The Raman and infra-red spectra of the 1 : 3- and 1 : 4-stereoisomerides do not show any resemblance to those of 1 : 1-dimethyl*cyclo*hexane, nor yet to those of the 1 : 2-derivatives previously examined (A., 1934, 345, 716). As regards the relation between Raman and infra-red spectra for any one compound, in some cases the same bands appear in both types of spectra, but not with the same intensity. In other cases important bands in one spectrum never appear at all in the other. Investigation of one spectrum alone, therefore, is not sufficient to give all the modes of vibration of these mols. M. S. B.

**Raman effect of methyl*cyclo*pentano derivatives.** M. Godchot, (Mlle.) G. Cauquil, and R.

Calas (Compt. rend., 1936, 202, 1129—1130).—Ketonic, alcoholic, and acetic ester derivatives possess the principal frequencies of the methyl*cyclo*pentane nucleus (cf. A., 1932, 559). Ketones and esters give the characteristic C:O frequency, 1744 cm.$^{-1}$ Corresponding optically active and racemic compounds have identical spectra. For the range 200—800 cm.$^{-1}$ there is a strong resemblance between the spectra of *cis*- and *trans*-alcohols, but not of the corresponding esters. M. S. B.

**Raman spectrum and constitution of pyrazole and of some of its derivatives.** G. B. Bonino and R. Manzoni-Ansidei (Atti R. Accad. Lincei, 1935, [vi], 22, 438—443).—Raman lines for pyrazole (I) and its Me derivatives are recorded. The spectrum of (I) contains 11 lines, similar to those of thiophen and pyrrole, but there are no lines characteristic of the double linking. O. J. W.

**Raman spectrum of dimethylfurazan and of dimethyloxdiazole.** R. Manzoni-Ansidei (Atti R. Accad. Lincei, 1935, [vi], 22, 444—447).—The Raman spectra of dimethylfurazan and of dimethyloxdiazole contain 21 and 18 lines, respectively (cf. A., 1933, 886). O. J. W.

**Raman spectrum of some substituted pyrrolealdehydes.** G. B. Bonino, R. Manzoni-Ansidei, and D. Dinelli (Atti R. Accad. Lincei, 1935, [vi], 22, 448—452).—The Raman spectra of the *C*-alkylpyrrolealdehydes investigated all show an intense diffuse line at 1620—1650 cm.$^{-1}$, which can be attributed to the strongly perturbed C:O group, and also a line at 1560—1570 cm.$^{-1}$, which does not occur in the spectrum of pyrrole-2-aldehyde and is probably due to a double linking. O. J. W.

**Light scattered by cloudy media and its polarisation.** H. von dem Borne (Z. Physik, 1936, 99, 73—102).—Scattering was investigated for smokes and vapours by means of a $Cu_2O$ cell at 0·55 and 1·0 μ. A scattering function was determined and applied to meteorological problems. A. B. D. C.

**Scattering of light in optical glasses.** R. S. Krishnan (Proc. Indian Acad. Sci., 1936, 3, A, 211—220).—The intensity and polarisation of the light scattered transversely by 17 optical glasses has been studied, with the incident light unpolarised, horizontally polarised, and vertically polarised. All the glasses gave a weak fluorescence. The depolarisation measurements indicate the presence of anisotropic mol. aggregates of size not small compared with the λ of light. L. J. J.

**Emission of ultra-violet radiation in the Reboul effect.** O. Viktorin (Compt. rend., 1936, 202, 941—943).—Very feeble radiation (2600—2000 A.) was detected with a photo-counter. H. J. E.

**Radiation emitted in the dehydration and hydration of quinine sulphate.** R. Audubert and M. Prost (Compt. rend., 1936, 202, 1047—1049; cf. A., 1935, 1055).—The ultra-violet radiation emitted on the dehydration on heating and hydration of quinine sulphate has been studied using a CuI photo-cell sensitive to 2000—2500 A. The emission accompanying hydration is 6—8 times that given on dehydration. The radiation comes from the surface layers, since it is independent of the thickness of the specimens used. A strong magnetic field has no effect. On dehydration of the salt the radiation is probably partly due to a modification in the crystal structure. The energy emitted on hydration is only $10^{-11}$—$10^{-12}$% of the heat of hydration. R. S. B.

**Phosphorescent beryllium nitride.** S. Satoh (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, 29, 41—46; cf. A., 1934, 741).—$Be_3N_2$ gives strong phosphorescence when mixed with $Al_2O_3$ and excited by a Hg-vapour lamp. The phosphorescence increases with the % of $Al_2O_3$ up to a max. at 30%, and does not occur without excitation. 2% of Ti and Zr confer no phosphorescence on $Be_3N_2$; 2% of Mn gives a feeble effect. The cathode-ray spectrum of $Be_3N_2+30\%$ $Al_2O_3$ is continuous at 4200—4900 A., with a max. at approx. 4650 A. The spectra of Be, $Be_2O_3$, and $Al_2O_3$ are very faint. R. S. B.

**Relations between luminescent power and lattice structure. I. Layered-lattice crystals.** A. Kutzelnigg (Angew. Chem., 1936, 49, 267—268).—A lecture. E. S. H.

**Fluorescence spectra of deuteroporphyrin and pyroporphyrin; fine structure, emission in the near infra-red.** C. Dhéré and O. Biermacher (Compt. rend., 1936, 202, 442—444).—The fluorescence spectrum of deuteroporphyrin in $Et_2O$ shows a principal band at 6230 A. and six other bands in the orange and red region. Pyroporphyrin shows analogous bands. Copro-, deutero-, and pyro-porphyrin show supplementary bands in the near infra-red of shorter λ than those of protoporphyrin. The infra-red fluorescence is probably due to photo-porphyrins produced by the irradiation. J. W. S.

**Carcinogenic action and absorption and fluorescence spectra of 1 : 2-benzpyrene.** C. Sannié (Biochem. J., 1936, 30, 704—706).—Ultra-violet absorption and fluorescence spectra of 1 : 2-benzpyrene, 4-keto-1′ : 2′ : 3′ : 4′-tetrahydro-1 : 2-benzpyrene, and β-1-pyrenoylpropionic acid in different solvents and in different states of purity, and of various fractions of Schroeter mixture, are given. It is unlikely that the fluorescence spectra characteristic of purified hydrocarbons would be recognisable in complex mixtures. H. D.

**Fluorescence spectrum of 1 : 2-benzpyrene.** W. V. Mayneord (Biochem. J., 1936, 30, 707—708).—The fluorescence spectrum of 1 : 2-benzpyrene is determined and the influence of impurities alleged by Sannié (see above) is denied. H. D.

**Inhibiting action of alkaloids on the fluorescent power of uranine in relation to the antioxidant properties of these substances.** A. Boutaric and J. Bouchard (Ann. Soc. Sci. Bruxelles, 1936, 56, B, 35—40).—A method for the comparison of the intensity of fluorescence of two different solutions is described. The diminution of the fluorescent power of uranine (I) by the action of different alkaloids at const. $p_H$ in aq. solution as salts, or in EtOH solution as free bases, is much $<$ by the action of the corresponding amine oxides, or genalkaloids (II), which are no longer antioxidants. The diminution in inhibiting action on the fluorescence of (I) apparently runs parallel with the disappearance of antioxidant properties in (II) and with the reduction in toxicity also observed. M. S. B.

**Becquerel effect and photochemical sensitivity of some fluorescent dyes.** (MLLE.) C. STORA (Compt. rend., 1936, **202**, 408—410).—It is concluded that the Becquerel effect and the photochemical sensitivity of a dye depend both on oxidation–reduction phenomena and on the presence of certain groups in the mol. The recovery of photosensitivity at the expense of the medium indicates the essential rôle played by the solvent. The same relation to fluorescence exists for the photo-voltaic effect as for photochemical sensitivity. J. W. S.

**Contact potential measurements on tungsten films.** D. B. LANGMUIR (Physical Rev., 1936, [ii], 49, 428—435).—Changes in contact potential, produced by varying the amount of Th on the surface and by varying the temp., were measured for a W filament by using a tube containing two filaments. Electron emission with very low accelerating fields is compared with the contact potential on the same surface and at the same temp.; the theoretical law is obeyed but not for higher fields or with differences of temp. An increasingly negative contact potential is shown with rising temp., the activated surface having the larger rate of change. Pure W shows a temp. coeff. of opposite sign, indicating a decreasing work function with rising temp. N. M. B.

**Photo-electric electron yield with counter tubes.** W. CHRISTOPH (Physikal. Z., 1936, **37**, 265—269).—Counter tubes fail to register all the electrons emitted from the cathode. Increase in field strength gives an increase in photo-electric yield, and this increase is greater when the irradiating light is of longer λ. The difference between electrons counted and those emitted is the greater, the smaller is the difference between the limiting λ of the metal concerned and the λ of the incident light. A. J. M.

**Surface photo-electric effect in metals. II.** K. MITCHELL (Proc. Roy. Soc., 1936, **A**, **153**, 513—533).—Theoretical. Spectral distribution curves for (*a*) polarised and (*b*) unpolarised light, and (*c*) energy distribution curves are calc. (*b*) show excellent agreement with experimental results for alkali metals, and (*c*) agree with Brady's results (A., 1935, 4). L. L. B.

**Electrical evidence on calcite imperfection.** F. C. FRANK (Nature, 1936, **137**, 656—657; cf. this vol., 404).—Joffé's work on electrical conduction in calcite (Ann. Physik, 1923, 72, 473) indicates the existence of lattice spaces unfilled by $Ca^{\cdot\cdot}$ ions, affecting the val. of *e*. L. S. T.

**Influence of the nature and position of groups on the photo-potential of substituted aromatic amines.** (MLLE.) H. T. NGA (Compt. rend., 1936, **202**, 1049—1050; cf. A., 1935, 1463).—The photo-potential given by 0·05*N* solutions of *o*-, *m*-, and *p*-Me, $-NO_2-$, and -halogen derivatives of $NH_2Ph$ in 0·005*N* aq. KI, KCl, $K_2SO_4$, $CuSO_4$, $HCO_2Na$, and $KClO_3$ at 18° have been measured, using a Hg-vapour lamp for excitation. The quantities of energy absorbed by the various compounds are approx. the same, and all, except $C_6H_4I\cdot NH_2$, are stable during the experiment. The photo-effect increases from *o* to *m*, but *m* and *p* are identical. A parallel is drawn between the photo-voltaic effect and chemical reactivity. R. S. B.

**Effects of heat and ultra-violet light on the rectifying action of some crystals.** B. K. SEN (Indian J. Physics, 1936, **10**, 91—102).—The action of heat and ultra-violet light on the rectifying properties of pyrolusite, galena, Cu pyrites, zincite, "Master" crystal, and particularly Fe pyrites has been investigated. The rectifying power diminishes with rise of temp., but, contrary to Khastgir *et al.* (A., 1935, 12, 682), does not disappear entirely below 200°. Irradiation of the crystal with ultra-violet light causes an increase in conductivity of all crystals examined, but the effect on rectification was small. A. J. M.

**Photo-electric barrier layer effect.** R. DEAGLIO (Atti R. Accad. Sci. Torino, 1934, **70**, I, 272—275; Chem. Zentr., 1935, ii, 1137).—A Ag–$Cu_2O$ single-crystal contact rectifier showed no photo-electric barrier-layer effect, indicating the independence of the photo-electric and the unidirectional conduction effects. J. S. A.

**Changes in absorption of weak high-frequency electric fields by liquids as a function of the voltage of the field.** E. K. SAVOJSKI and B. M. KOSIREV (Compt. rend. Acad. Sci. U.R.S.S., 1936, **1**, 109—113).—The absorption curve for AcOH shows a series of step-like discontinuities with increasing field strength. They do not depend on temp. (18—25°) or on the [AcOH]. H. J. E.

**Changes of absorption of weak electric fields of high frequency in certain substances as a function of the strength of these fields. II.** E. K. SAVOJSKI and B. M. KOSIREV (Compt. rend. Acad. Sci. U.R.S.S., 1936, **1**, 219—220).—The crit. strengths of the high-frequency field in the range 130—180 volts per cm. in liquid AcOH persist in the solid, indicating that their existence is due to some intramol. process. The no. and val. of crit. potentials in the range 375—480 volts per cm. are the same in solid AcOH and NaOAc. N. M. B.

**Electric spark discharge in insulating liquids.** F. KOPPELMANN (Z. tech. Physik, 1935, **16**, 125—141; Chem. Zentr., 1935, ii, 979).—A comprehensive review of the phenomena and theory of the discharge. J. S. A.

**Spectral distribution of the depolarisation current for *X*-irradiated KCl crystals.** N. KALABUCHOV and J. KURSCHEV (Z. Physik, 1936, **99**, 254—258).—The spectral distribution curve has two max. at 570 and 630 mμ; the first indicates a level 1·86 volts above the conducting zone, and the second is ascribed to a level associated with $K^+$ ions. A. B. D. C.

**Electrical conductivity of thin films of rubidium on [Pyrex] glass surfaces.** A. C. B. LOVELL (Nature, 1936, **137**, 493—494).—The resistivity of films a few atoms thick deposited at 64—90° abs. is somewhat > that of the metal in bulk, but different from that previously reported. L. S. T.

**Electret.** H. NUMAKURA (J. Electrochem. Assoc. Japan, 1935, **3**, 89—92).—An electret is formed by solidifying a mixture of rosin with ceresin or beeswax, or of ceresin with mastic or dammar, etc., in an electric field of 2 kv. per cm. The charges on surfaces cut perpendicular to the electric field are due to orientation of the polar mols. during solidification. The property disappears on heating for 24 hr. at 55°. H. J. E.

**Relation between electrical conductivity and the coefficient of internal friction in melted salts.** S. KARPATSCHEV and A. STROMBERG (J. Phys. Chem. U.S.S.R., 1934, **5**, 1283—1291).—A theoretical relationship between the conductivity, internal friction, mol. wt., and *d* is derived. Experimental vals. for the alkali and Ag halides and nitrates are 1·4—2·2 times too large. CH. ABS. (*e*)

**Theory of electrolytic conduction and diffusion in crystals. III. Calculation of energies of disarray and threshold energies. Effect of pressure on electrolytic conduction.** W. JOST and G. NEHLEP (Z. physikal. Chem., 1936, **B**, **32**, 1—21; cf. A., 1934, 949).—The previous calculations of energy of polarisation and disarray (*ibid.*, 11) have, by taking account of the displacement of the ions in the vicinity of a point of disarray, been so far improved and rendered more precise that it is possible to decide in a particular case whether the disarray consists in the presence of ionic voids of one sign together with an equiv. no. of ions in the intra-lattice space or the presence of equiv. nos. of voids of both signs (cf. A., 1935, 1302, 1305). It appears certain that the disarray in lattices of salts with ions of similar size and polarisability and not too large dielectric consts. is of the second type. Owing to the considerable effect of repulsive forces on the threshold energy which must be exceeded for migration of a void to be possible, the conductivity must be measurably influenced by pressure, the magnitude of the effect depending on which type of disarray is involved. R. C.

**Direct-voltage experiments with electrolytically produced aluminium oxide.** G. FRANCKENSTEIN (Ann. Physik, 1936, [v], **26**, 17—54).—The dielectric properties of electrolytically produced films of $Al_2O_3$ (thickness 10—100 $\mu$) were investigated using d.c. The surface conductivity does not depend on the structure or method of prep. of the film, but on the humidity of the atm. by an exponential law. The methods by which $H_2O$ is taken up by the surface are discussed. The conductivity through the film depends on the method of prep. Conductivity increases exponentially with the voltage, and is diminished by drying. It is impossible to remove $H_2O$ completely from thick films. The resistance varies linearly with thickness for thin layers, and exponentially for thick ones. For thin layers, electrical breakdown occurs across air in the pores of the film, but for thick films breakdown is thermal. The breakdown potential is not affected by humidity. Investigation of after-effects showed the existence of a considerable back-current and back-e.m.f., decaying exponentially with time. A. J. M.

**Polarisation of liquids and their saturated vapours in the critical temperature region.** J. MARSDEN and O. MAASS (Canad. J. Res., 1936, **14**, **B**, 90—95; cf. this vol., 139).—The polarisations of the liquid and the saturated vapour of MeOEt and $C_3H_6$ are identical at the crit. temp. The liquid polarisation is a const. below the crit. temp., whilst that of the saturated vapour decreases according to a characteristic curve. R. S.

**Magnetic change of the dielectric constant of liquids.** A. PIÉKARA and M. SCHÉRER (Compt. rend., 1936, **202**, 1159—1160; cf. A., 1935, 1192).—A correction. The apparatus previously employed has been altered to reduce condenser deformation and the vals. obtained for $\Delta\varepsilon \times 10^4$ are now all $<$ the following: $C_6H_6$ 5, $CCl_4$ 3, PhMe 3, $CS_2$ 5. M. S. B.

**Dielectric constant of a space containing electrons.** S. P. PRASAD and M. N. VERMA (Z. Physik, 1936, **99**, 552—561).—The dielectric const. increases with electron concn. and with decreasing $\lambda$. A. B. D. C.

**Molecular interactions and structure of liquids.** P. GIRARD and P. ABADIE (Compt. rend., 1936, **202**, 398—400; cf. A., 1935, 1187).—The time of relaxation–concn. curves for solutions of $H_2O$ in dioxan and of dichlorohydrin in $C_6H_6$ show max. at low concns., suggesting that the semi-cryst. state appears when the ratio of electrostatic energy to thermal agitation attains a definite val. Applying Martin's equation (A., 1934, 1063) for the change in energy of a dipole in passing from one medium to another, to the max. of these curves, values of $\Delta w$ are about $3 \times 10^{-15}$ erg for most mols. The extrapolated val. for pure $H_2O$ is $4 \times 10^{-14}$ erg, equal to the energy of mol. agitation, whilst for other mols. it is less. Hence the semi-cryst. state of liquid $H_2O$ is highly developed at room temp. J. W. S.

**Anisotropy of the optical polarisation field in liquids. I, II.** B. S. R. RAO (Proc. Indian Acad. Sci., 1936, **3**, **A**, 240—243, 244—248).—I. Data are recorded for the variation of refractive index with temp. for $CS_2$, $C_6H_6$, $C_6H_{14}$, and $CCl_4$. $R_L$ is independent of temp. in the case of $CCl_4$, but in the other cases increases with rise of temp., showing that the optical polarisation field is anisotropic.

II. The consts. of anisotropy are calc., and the temp. dependence of the depolarisation of the scattered light deduced, from the above data. L. J. J.

**Birefringence by mechanical deformation of pure liquids.** C. SADRON (Compt. rend., 1936, **202**, 404—406; cf. Vorländer and Walter, A., 1926, 110).—Repetition of measurements on $C_7H_{15}\cdot OH$ and $C_8H_{17}\cdot OH$, using velocities of drum rotation well below the crit. velocity, yielded vals. of 4·5 and 6·5 ($\times 10^{-12}$), respectively, for their dynamic birefringences. Raman and Krishnan's theory (A., 1928, 573) predicts $7{\cdot}4 \times 10^{-12}$ for $C_7H_{15}\cdot OH$. The vals. for oleic acid, cinnamaldehyde, $C_{12}H_{25}\cdot OH$, and $CH_2Ph\cdot OH$ are 360, 51·6, 29·6, and 17·5 ($\times 10^{-12}$), respectively. J. W. S.

**Electro-optical Kerr effect in methane, ethylene, and ethane.** W. M. BREAZEALE (Physical Rev., 1936, [ii], **49**, 625—626; cf. A., 1935, 1192).—Measurements of the Kerr effect were made at 6500 A., pressures 30—100 atm., and temp. 15—55°.

Results, with the aid of the Langevin–Born theory, give for the Kerr const. at n.t.p. and 6500 A., the vals. $\times 10^{12}$: $CH_4$ 3·66, $C_2H_2$ 16·3, and $C_2H_4$ 10·4.
N. M. B.

**Curves of constant affinity in the phase changes of single substances.** J. E. VERSCHAFFELT (Bull. Acad. roy. Belg., 1936, **22**, [v], 252—264).—Theoretical.
D. R. D.

**Theory of homopolar valency. Significance of the fission rule for olefines and radicals.** O. SCHMIDT (Z. Elektrochem., 1936, **42**, 175—184; cf. A., 1932, 716; 1935, 1286).—The wave-mechanical treatment of homopolar valency is inferior to the statistical method in which the direction of the electron spin is taken into account. The question is discussed with reference to the thermal decomp. of olefines and radicals.
F. L. U.

**Use of a Geiger–Müller counter for the study of the diffraction of *X*-rays by a gas.** W. VAN DER GRINTEN and H. BRASSEUR (Nature, 1936, **137**, 657).—Replacement of the photographic plate by a Geiger–Müller counter gives good results for the Cl-Cl distance in $CCl_4$.
L. S. T.

**Peculiarities of water and aqueous solutions.** H. ULICH (Angew. Chem., 1936, **49**, 279—282).—A discussion of the anomalies mainly linked with association.
E. S. H.

**Condensed helium at absolute zero.** F. LONDON (Proc. Roy. Soc., 1936, **A**, **153**, 576—583).—The usual methods of lattice theory cannot be applied to the He lattice, owing to the fact that its zero point energy is of the same order of magnitude as the interaction energy, and has a decisive effect on the constitution of the lattice. The fact that closest packed structure is stable only under pressure explains why solid He can only exist, even at 0° abs., under pressure. If no external pressure is applied, a configuration with the co-ordination no. 4 is shown to have considerably lower energy, and gives a rough model of the liquid modification of He which is stable at 0° abs.
L. L. B.

**The liquid state and interatomic forces. I, II.** S. FRANCHETTI (Atti R. Accad. Lincei, 1935, [vi], 22, 433—438, 585—593).—Mathematical and theoretical.
O. J. W.

**Symmetry of a crystal lattice and its electron levels.** F. HUND (Z. Physik, 1936, **99**, 119—136).—Qual. rules are deduced to determine whether or not a crystal is an insulator.
A. B. D. C.

**The three-centre problem. II.** G. S. GORDADSE (Z. Physik, 1936, **99**, 287—299; cf. A., 1935, 1298).—Mathematical. The results are used to obtain energy formulæ for $H_2^+$ and $H_3^{++}$.
A. B. D. C.

**Accommodation coefficient of deuterium.** W. B. MANN and W. C. NEWELL (Nature, 1936, **137**, 662).—The accommodation coeffs. of $H_2$, 99·2% $D_2$, and He relative to a Pt wire at 100·7°, with the surrounding gas at approx. 16°, are 0·24(3), 0·30(8), and 0·29(4), respectively.
L. S. T.

**Hydrogen atoms.** V. BARGMANN (Z. Physik, 1936, 99, 576—582).—Pauli's matrix equation for H leads to Fock's results (cf. this vol., 266).
A. B. D. C.

**Concentration of deuterium in organic compounds. II. General discussion with particular reference to benzene.** M. DOLE (J. Amer. Chem. Soc., 1936, **58**, 580—585; cf. A., 1934, 853).—A crit. review of published work. The at. wt. of H in org. compounds is considered to be more nearly normal than has been suspected hitherto.
E. S. H.

**Vibrations of tetrahedral pentatomic molecules. V. General criteria for potential functions.** (MISS) J. E. ROSENTHAL (Physical Rev., 1936, [ii], 49, 535—537; cf. A., 1934, 1293).—If the forces along the linkings of the $YX_4$ mol. are fairly large compared with "interaction forces," the ambiguity in the vals. of the consts. in the potential energy function is removed. The ratio of the masses of the Y and X atoms determines the chemically correct set of force consts. Limiting vals. of the const. for the Y·X linking in $CH_4$, $CCl_4$, $TiCl_4$, $SiCl_4$, $SnBr_4$, $SO_4''$, and $ClO_4'$ are given.
N. M. B.

**Vibration–rotation energy levels of polyatomic molecules. I. Mathematical theory of semi-rigid asymmetrical top molecules.** E. B. WILSON and J. B. HOWARD (J. Chem. Physics, 1936, 4, 260—268).—Mathematical.
L. J. J.

**Minimum potential for ozone formation by electron collision.** F. KRÜGER and C. ZICKERMANN (Z. Physik, 1936, 99, 428—452).—This min. potential is 6·3 volts, and indicates that $O_2$ has to be dissociated into one excited and one non-excited O atom for formation of $O_3$.
A. B. D. C.

**Significance of electron collision experiments with CO and bond energy values of C·C and H·C from the assumption D(CO)=6·9 volts.** R. SCHMID (Z. Physik, 1936, 99, 274—280).—The crit. potential of CO gives the dissociation energy of 6·9 volts, and this gives 3·76 volts per C·C linking, and 4·4 volts per C·H linking.
A. B. D. C.

**Dissociation products of the CN molecule assuming a dissociation energy of 6·9 volts for CO.** R. SCHMID (Z. Physik, 1936, 99, 562—568).—A dissociation energy of 6·9 volts for CO gives CN dissociating into C ($^5S$)+N ($^4S$) atoms at 8·15 volts.
A. B. D. C.

**Calculation of rotation energy constants of molecules from a formula and its application to the calculation of dissociation energies.** E. A. HYLLERAAS (Naturwiss., 1936, 24, 279—280).—A formula is derived and applied to the calculation of the dissociation energy of the CdH mol.
A. J. M.

**Rotation of molecules in fields of octahedral symmetry.** A. F. DEVONSHIRE (Proc. Roy. Soc., 1936, **A**, **153**, 601—621).—Mathematical. The solution of Schrödinger's equation for a diat. mol. rotating in a field of octahedral symmetry is discussed.
L. L. B.

**Absolute value of C·H linking moment, and sign of charge of the hydrogen atom in organic carbon compounds.** H. G. TRIESCHMANN (Z. physikal. Chem., 1936, **B**, **32**, 22—26).—From calculation of the approx. moments of the aliphatic C·H and C·Cl linkings it seems probable that the H in the C·H linking is negative (cf. this vol., 268).
R. C.

**Nature of the chemical binding of certain oxides and sulphides.** P. K. Sen-Gupta (J. Univ. Bombay, 1935, 4, Part II, 74—82).—From the infra-red absorptions of ZnS, ZnO, CdS, CdO, HgS, CaO, SrO, and BaO it is concluded that the linking is ionic in nature (cf. A., 1934, 237). J. W. S.

**Ferromagnetic saturation moment.** L. Néel (Compt. rend., 1936, 202, 1269—1272).—Theoretical. The discrepancy between observed saturation moment and that calc. from the Curie const. can be explained by incomplete orientation of magnetic moments at saturation, due to coupling between atoms being intermittent and subject to statistical laws. L. J. J.

**Cavitation and surface tension. II.** F. K. T. van Iterson (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 330—339).—The theory of the appearance and disappearance of small bubbles when $H_2O$ containing air passes a convergent–divergent constriction in a tube is discussed. In the divergent portion the bubbles disappear suddenly and the resultant shock erodes the walls, as in pumps. It is shown that oil increases the contact angle for air–steel from 22·5° to 90°, the air bubbles becoming hemispherical on a greasy surface. Oil increases cavitation owing to the decrease in $\sigma$ for air–$H_2O$ and the increase in $\sigma$ for air–wall, both effects increasing the adhesion of the bubble to the wall. R. S. B.

**Quantitative determination of scattering of *X*-rays by microcrystalline layers.** J. Brentano (Z. Physik, 1936, 99, 65—72).—Experimental details are discussed. A. B. D. C.

**Scattering of *X*-rays from amorphous substances and their molecular distribution.** M. Ogura (Sci. Rep. Tôhoku, 1936, 24, 587—594).—The Debye–Menke method (A., 1930, 1350; 1932, 986) of calculating mol. distribution in amorphous substances is applied to polyat. compounds. M. S. B.

**External form of the crystal and its effect on the interference phenomena of the space lattice.** M. von Laue (Ann. Physik, 1936, [v], 26, 55—68).—Theoretical. Effects of the external form of a crystal on the sharpness of the interference pattern are observed with electron diffraction, but not with *X*-rays. The elementary theory of space-lattice interference is extended to take this into account, and the general laws governing the intensity in the neighbourhood of the interference spots are derived. The theory is applied to the observations of Kirchner *et al.* (A., 1935, 1451). A. J. M.

**Energy levels of electrons in a one dimensional lattice with localised defects (" Lockerstellen "). Application to electric discharge.** A. Sokolov and N. Machalova (Z. Physik, 1936, 99, 503—517).—Localised defects give levels in the normally " forbidden " zone. These are dependent on the potential energy associated with the defects and the electron energy; they explain discharge through dielectrics. A. B. D. C.

**Growth and structure of electrolytically prepared aluminium oxide layers.** T. Rummel (Z. Physik, 1936, 99, 518—551).—Highly insulating layers > 1 $\mu$ thick have been obtained free from corrosion. Their dielectric properties are largely dependent on the hydroxide content. A. B. D. C.

**Surface layers of crystals.** (Sir) J. Larmor (Nature, 1936, 137, 575—576). L. S. T.

**The Beilby layer.** G. I. Finch and A. G. Quarrell (Nature, 1936, 137, 516—519).—A review. L. S. T.

**Influence of temperature on asterism of crystals.** S. Dembicka (Acta phys. polon., 1933, 2, 285—290; Chem. Zentr., 1935, ii, 1132).—The asterism of slightly deformed Al, NaCl, and $CaSO_4$ crystals was unaffected by temp. In the case of Al, asterism disappeared on recrystallisation at higher temp. J. S. A.

**Röntgenographic detection of lattice deformation in cold-deformed nickel.** W. E. Schmid and E. A. W. Müller (Z. tech. Physik, 1935, 16, 161—164; Chem. Zentr., 1935, ii, 972).—From measurements of the intensity, line breadth, and lattice spacing of the (024) reflexion from Ni, a relation is derived between deformation, applied stress, and compressibility. Inner stresses are calc. J. S. A.

***X*-Ray diffraction study of liquid sodium.** L. P. Tarasov and B. E. Warren (J. Chem. Physics, 1936, 4, 236—238).—The radial distribution of atoms about any atom in liquid Na at 103° has been determined by Fourier analysis of the scattering curve for monochromatic Mo $K\alpha$ radiation. The distribution curve is essentially a smoothed-out distribution curve for the cryst. phase, showing concns. at 4·0 and 7 A., and a dip at 5·0 A. L. J. J.

**Distribution of impurities on crystallisation.** D. D. Saratovkin (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 323—326).—The conditions controlling the separation of impurities in the layers between crystallites are discussed and are applied to the slow melting of impure ice, the formation of Widmannstätten structures (system Fe–C), of etch figures, and of dendritic crystals. With the crystallisation of $Na_2S_2O_3$ in presence of $CoCl_2$ as added impurity the coloured intermediate layers of impurity could be observed. R. S. B.

**Effect of naphthalene-2-sulphonic acid on the crystallisation of copper sulphate pentahydrate.** F. Barillet (Compt. rend., 1936, 202, 1194—1195).—Crystallographic data are given for the $CuSO_4,5H_2O$ crystals separated from solutions of const. Cu content containing varying proportions of 2-$C_{10}H_7$·$SO_3Na$. M. S. B.

**Modifications of the crystal faces of uric acid by the addition of dyes to the mother-liquor.** P. Gaubert (Compt. rend., 1936, 202, 1192—1194).—Considerable deviations from the original cryst. forms are produced and the character of the deviations varies with the dye. The polychroism of the crystals and the distribution of the dye between crystals and mother-liquor indicate that solid solutions are formed. M. S. B.

**Structure of $CuAl_2$.** A. K. Trapeznikov (J. Phys. Chem. U.S.S.R., 1934, 5, 1177—1185).—The structure proposed by Owen and Preston (A., 1924, ii, 111) is not supported by *X*-ray data. The lattice consts. are *a* 6·054±0·003, *c* 4·87$_4$ A.; symmetry classes $V^d$, $C_4^v$, $D_4^h$. Bradley and Jones' data are confirmed (cf. A., 1933, 454). CH. ABS. (*e*)

**Crystal structure of $Fe_3Ti$.** W. JELLINGHAUS (Z. anorg. Chem., 1936, **227**, 62—64).—*X*-Ray powder diagrams of Fe with 24% Ti gave *a* 5·19 A., *c/a* 1·57, and a tetragonal lattice. Since, assuming that the unit cell contains four mols. of $Fe_3Ti$, the calc. *d* agrees fairly with that of an alloy of the same composition, it is inferred that such alloys contain the compound $Fe_3Ti$. This conclusion is supported by the fact that the lattice of $Al_3Ti$ is also tetragonal. F. L. U.

**Crystal structure of chlorine.** W. H. KEESOM and K. W. TACONIS (Physica, 1936, **3**, 237—242, and Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 314).—Data obtained at −185° with the *X*-ray goniometer (A., 1935, 839) are recorded. They give a tetragonal lattice with *a* 8·56 and *c* 6·12 A.; *d* 2·09, 8 mols. per unit cell. Intensities of Debye–Scherrer lines agree with the space-group $D_{4h}^{16}$, and the Cl—Cl distance in $Cl_2$ 1·99 A. L. J. J.

**Structure of ice III.** R. L. McFARLAN (J. Chem. Physics, 1936, **4**, 253—259).—*X*-Ray diffraction measurements at −155° give a body-centred orthorhombic structure, with *a* 10·20, *b* 5·87, *c* 7·17 A. The space-group is $V_h^{26}$—*Ibam*, with 16 mols. in the unit cell, giving *d* 1·105. Each O'' ion is surrounded by a distorted tetrahedron of O'' ions; H˙ ions are assumed to lie midway between pairs of neighbouring O'' ions. The mechanism of the transition between the different forms of ice is discussed. L. J. J.

**Nature of lattice disarray in silver bromide.** C. WAGNER and J. BEYER (Z. physikal. Chem., 1936, B, **32**, 113—116).—Measurements of *d* and the lattice const. at 410° have indicated that the electrical conductivity is due to Ag˙ ions moving into the spaces between the lattice points and leaving their normal positions vacant; there are no vacant positions in the anion lattice. R. C.

**Basic salts. XIII. Constitution of solid basic salts of bivalent metals. I. Basic cobalt halides with single-layer lattice.** W. FEITKNECHT (Helv. Chim. Acta, 1936, **19**, 467—474).—Lattice dimensions have been determined for $CoCl_2,3Co(OH)_2$, $CoBr_2,3Co(OH)_2$, and the corresponding mixed basic halide. They all possess single-layer lattices, *i.e.*, there is a statistical exchange of OH' with halide ion. Replacement of Cl' by Br' causes a marked extension of the lattice. Replacement of OH' by halide ion produces a small extension only in the single-layer lattice, but a large one in the double-layer type. M. S. B.

**Structure of cupric ammonium bromide.** A. SILBERSTEIN (Compt. rend., 1936, **202**, 1196—1197).—The vals. of the parameters *u*, *v*, and *w* of the structure of $CuBr_2,2NH_4Br,2H_2O$ (cf. this vol., 143) have been calc. by comparison with the isomorphous $CuCl_2,2NH_4Cl,2H_2O$ and interat. distances are given. The salt is complex and $H_2O$ enters into the formation of the complex ion $[CuBr_4(H_2O)_2]''$, but in solution it reacts as a mixture of its constituent salts. M. S. B.

**Structure and alterations of structure of NiS and NiSe.** G. R. LEVI and A. BARONI (Z. Krist., 1936, **92**, 210—215).—Various forms of NiS have been prepared and studied by *X*-rays and electron diffraction methods. γ-NiS is identical with millerite (rhombohedral); β-NiS is the usual synthetic compound (hexagonal). The crystallinity is ill-defined, and grows with time. α-NiS is amorphous and unstable in air. The transition γ-NiS to β-NiS is studied. Analogous properties are shown by the selenides. B. W. R.

**Structure determinations of the complex sulphides. I. Structure of tin sulphide SnS and teallite $PbSnS_2$. II. Crystal chemistry of the sulpho-salts of arsenic, antimony, and bismuth.** W. HOFMANN (Z. Krist., 1935, **92**, 161—lxx, lxx—185).—I. SnS is rhombic, 4 mols. in cell, $a_0$ 3·98, $b_0$ 4·33 $c_0$ 11·18 A., space-group $V_h^{16}$. Parameters are determined completely from intensity measurements; the structure is a deformed galena structure. Teallite is rhombic, $a_0$ 4·04, $b_0$ 4·28, $c_0$ 11·33 A., with similar structure.

II. The position of the S with reference to the metal atom is discussed and the chains of $SbS_3$ pyramids are further described. The existence in needle-like crystals of further chains of $SbS_3$ and $BiS_3$ pyramids, $PbS_6$ octahedra, and $CuS_4$ and $FeS_4$ tetrahedra is suggested. B. W. R.

**Crystallographic structure of isomorphous compounds $(M^{IV+})P_2O_7$.** G. R. LEVI and G. PEYRONEL (Z. Krist., 1936, **92**, 190—209).—The structure of compounds $M^{IV}P_2O_7$ (M=Si, Ti, Sn, Zr, Hf) has been determined in order to find the shape of the radical $(P_2O_7)^{IV-}$. All these pyrophosphates are cubic, space-group $T_h^6$, 4 mols. in cell. Vals. of $a_0$ and *d* are given. Exact at. distances for the P and O atoms are given, based on intensity measurements. $Hf^{IV+}$ is found to have a slightly smaller at. radius than $Zr^{IV+}$. B. W. R.

**Rotation of anionic polyhedra in cubic crystals. I. Perchlorates.** C. FINBAK and O. HASSEL (Z. physikal. Chem., 1936, B, **32**, 130—134).—Examination of the high-temp. structures of $NaClO_4$, $KClO_4$, and $NH_4ClO_4$ by means of powder diagrams has yielded results which are irreconcilable with those of Herrmann and Ilge (A., 1930, 528) or of Braekken and Harang (A., 1931, 549) and are explained more satisfactorily by assuming that the $ClO_4'$ in these lattices are capable of rotation, than by supposing the O to occupy fixed positions. R. C.

**Crystal structure of magnesium and nickel antimonates.** J. BEINTEMA (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 241—252).—*X*-Ray measurements indicate the structure $[M(H_2O)_6][Sb(OH)_6]_2$, where M=Mg or Ni. The following data are given for the Mg and Ni compounds, respectively: *a* 16·079, 16·019, *c* 9·841, 9·768 A.; vol. of unit cell (6 mols.) 2203, 2171×$10^{-24}$ c.c.; $d_{calc.}$ 2·633, 2·802; $d_{obs.}$ 2·598, 2·77; space-group $D_{3d}^1$. O. J. W.

**Structures and formulæ of the Prussian-blues and related compounds.** J. F. Keggin and F. D. Miles (Nature, 1936, **137**, 577—578).—The at. arrangements in the cubic structures, obtained from *X*-ray analysis, are outlined. In Prussian-blues, $Fe^{III}RFe^{II}(CN)_6$ where R is Na, K, Rb, or $NH_4$, *a* is 10·2 A., and in "Ru-purple," in which Ru replaces $Fe^{\cdot\cdot}$, *a* is 10·4 A. The white ferrocyanides $Fe^{II}R_2Fe^{II}(CN)_6$, where R is Na, K, Rb, Cs, or $NH_4$, have *a* 5·1 A. and form a series closely related to the above. Berlin-green, $Fe^{III}Fe^{III}(CN)_6$, the oxidation product of Prussian-blue, has *a* 5·1 A., and *cupriferricyanides*, $Cu^{II}RFe^{III}(CN)_6$ have *a* slightly $<$ 10·2 A. All structures are similar, but between the members of each class the difference in size of the alkali ions produces a slight variation in the lattice spacings. *Blues* containing no alkalis have been prepared, and the cubic Fe–(CN) skeleton has *a* 10·2 A. approx.

L. S. T.

**Influence of structure on the explosive properties of organic compounds.** V. V. Vasilevski, F. I. Bloschtein, and B. D. Kustrja (J. Gen. Chem. Russ., 1935, **5**, 1652—1667).—The space model of the mol. of 2 : 4 : 6-trinitrobenzazide (I) shows that its existence is compatible only with a ring structure for the $\cdot N_3$ group. The prep. of (I), $BzN_3$, and *o*- and *m*-nitrobenzazide is described, and m.p., *d*, *n*, and solubility data are recorded. The above azides undergo thermal decomp. to yield carbimides, the heat of decomp. of the $\cdot N_3$ group being 70·2 kg.-cal.

R. T.

***X*-Ray investigation of the crystals of benzoin.** M. Prasad and J. Shanker (J. Indian Chem. Soc., 1936, **13**, 123—127).—The unit cell, which contains 4 mols., has *a* 18·75, *b* 5·72, *c* 10·46 A., β 106° 50½′, space-group $C^5_{2h}$; the axial ratio agrees fairly well with the val. recorded in Groth's treatise.

C. R. H.

***X*-Ray diffraction intensity of the two liquid phases of *p*-azoxyanisole.** G. W. Stewart (J. Chem. Physics, 1936, **4**, 231—236).—The intensity distribution curve for the liquid crystal at 125° resembles that of the transparent liquid at 150°, but has a narrower peak, with greater max. intensity and steeper slope on the zero-angle side. The regularity of structure in the liquid-crystal swarms of $10^5$—$10^6$ mols. is $>$ that in the cybotactic groups of 25—50 mols. in the liquid. The swarms tend to set their mol. axes perpendicular to the temp. gradient.

L. J. J.

**Crystallographic relationships between isomerides (ephedrine and *ψ*-ephedrine) and between *dl*-compounds and their components.** B. Gossner and H. Neff (Neues Jahrb. Mineral., A, 1935, **69**, Beil.-Bd., 347—363; Chem. Zentr., 1935, ii, 997—998; cf. A., 1935, 152).—Crystallographic data are given for *α-ψ*-, *dl-ψ*-, *l*-, and *dl*-ephedrine, *l*-, *dl*- (not a racemate but a *dl*-mixture), and *α-ψ*-methylephedrine.

H. N. R.

**Diffraction of *X*-rays by Bence-Jones protein.** A. Magnus-Levy, K. H. Meyer, and W. Lotmar (Nature, 1936, **137**, 616—617).—The spacings and intensities recorded for the cryst. protein are similar to those of oxyhæmoglobin (A., 1935, 687). The unit cell is large and should contain at least one "chemical" mol. of protein.

L. S. T.

***X*-Ray studies of crystallite orientation in cellulose fibres. II. Synthetic fibres from bacterial cellulose membranes.** W. A. Sisson (J. Physical Chem., 1936, **40**, 343—359; cf. A., 1935, 286).—From an *X*-ray study of cellulose membranes synthesised from various sugars by *Acetobacter xylinus*, and subjected to different kinds of mechanical treatment, it is inferred that the crystallites are oriented with the chain-axes parallel to the direction in which the sample is elongated, and that the (101) planes are oriented normal to the direction in which it is constricted. Further, the crystallites possess a major orienting tendency with reference to the chain-axis, and a minor or selective one with reference to the (101) plane.

F. L. U.

**Structure and properties of "byssus" or silk of oysters.** G. Centola (Gazzetta, 1936, **66**, 71—80).—The chemical and *X*-ray investigation of byssus (in its natural state, and stretched) shows that it consists of a mixture of chains of complex (keratin type) and chains of simple (silk fibroin type) $NH_2$-acids. It is the only natural fibre in which the mols. have no orientation, and this accounts for its physical properties.

O. J. W.

**Crystal orientation in tooth-enamel.**—See this vol., 623.

**Diffraction of rapid electrons in crystallised rock-salt. II.** S. G. Pinsker and L. I. Tatarinova (Physikal. Z. Sovietunion, 1936, **8**, 602—625; cf. A., 1935, 1309).—In the investigation of the scattering of rapid electrons at NaCl crystals obtained from solutions of different concn. (1%, 0·5%, 0·2%) the type of diagram obtained varied with the concn. of the solution. The normal Debye pattern was obtained from crystals from the 1% solution, but those from the more dil. solutions gave mainly point diagrams, corresponding with single crystals. Intermediate types of pattern, consisting of Debye rings and irregularly placed spots, were also obtained. The theory is discussed, and the application of the results to the study of thin crystal sheets is described.

A. J. M.

**Determination of atomic distances in the thallium and tellurium halides by electron diffraction.** W. Grether (Ann. Physik, 1936, [v], **26**, 1—16).—The separation of the atoms in TlCl, TlBr, TlI, $TeCl_2$, and $TeBr_2$ has been determined by electron diffraction experiments with their vapours. For TlCl, TlBr, and TlI the respective distances are 2·55, 2·68, and 2·87 A. For the distances Te–Cl and Te–Br the vals. are 2·36 and 2·49 A., respectively. It is not possible to decide whether the mols. of $TeCl_2$ and $TeBr_2$ are linear or bent, but if they are bent the angle is $>$150°. There is good agreement with results obtained from band spectra.

A. J. M.

**(A) Effects accompanying the diffraction of low-speed electrons. (B) Penetration of low-speed diffracted electrons.** H. E. Farnsworth (Physical Rev., 1936, [ii], **49**, 598—605, 605—609; cf. A., 1932, 789; 1933, 761).—(A) Investigation of the effect of density and arrangement of atoms in the surface plane on the fine structure of electron diffraction beams from a Ag single crystal, made by observing the structure of the diffraction beams corresponding with Bragg reflexions from two sets of planes for two different boundary planes of the crystal, show that the changes in fine-structure characteristics due to a change in the surface at. layer are small compared with the differences in those of the beams from different sets of at. planes. A new type of directional effect, showing a dependence of beam structure on the direction of the diffracted beam in the crystal, was observed.

(B) A known no. of at. layers of Ag was deposited on the surface of single crystals of Cu and Au by evaporation in vac. The no. of at. planes responsible for diffracting low-speed electrons was investigated by results for depth of penetration obtained from measurements on diffraction as a function of surface layer thickness for electron beams of different energies. $\nless$ 50% of the max. of each diffraction beam from a thick Ag crystal is due to the surface at. layer, and $\nless$ 90% to a surface layer two atoms thick.

N. M. B.

**Molecular structure of nitromethane from electron diffraction by the vapour.** C. DEGARD (Compt. rend., 1936, **202**, 1278—1280).—Two diffraction maxima are obtained, from which two mol. models are calc. The O—O distance does not correspond with the sum of the at. or ionic radii.

L. J. J.

**Variation with temperature of the piezo-electric effect in quartz.** A. PITT and D. W. R. MCKINLEY (Canad. J. Res., 1936, **14**, A, 57—65; cf. A., 1935, 1197).—The piezo-electric activity of quartz has been studied by static and dynamic methods between 4° and 813° abs. The activity, which decreases sharply by 10% below 5·5° abs., is const. up to 470°, above which it diminishes to zero at 813° abs. R. S.

**Magnetic behaviour in the chromium–sulphur system.** H. HARALDSEN and A. NEUBER (Naturwiss., 1936, **24**, 280).—Investigation of the susceptibility of Cr–S preps. over the concn. range CrS—$Cr_2S_3$ shows that there is a considerable increase in magnetism at a concn. corresponding with $CrS_{1\cdot175}$. This is analogous to the behaviour of Fe pyrites, which shows a max. in magnetisation at $FeS_{1\cdot12}$. The effect of temp. on the prep. of max. magnetisation was studied. Above 165° abs. it behaves as a ferromagnetic substance with a Curie point approx. 310° abs. There is a sudden decrease in magnetisation below 165° abs., a behaviour similar to, but more marked than, that of magnetite. A. J. M.

**New magnetostriction experiment.** J. L. SNOEK (Physica, 1936, **3**, 205—206).—Perrier's experiment (Helv. phys. Acta, 1935, **8**, 427) depends on the presence of a film of oxide, and is a variant of the Wiedemann effect. L. J. J.

**Arkadiev's method applied to elimination of skin effect and to investigation of dynamic magnetisation curves.** O. VELETZKAIA (Z. Physik, 1936, **99**, 569—575).—Magnetic permeability and loss curves, freed from skin effects, agree with the theory of magnetic viscosity for low field intensities and for audio and radio frequencies. A. B. D. C.

**Atomic theory of the magneto-caloric effect.** K. HONDA and T. HIRONE (Nature, 1936, **137**, 492).—The temp. changes of Fe, Ni, and Co with magnetisation, calc. by means of the Honda–Ôkubo theory of ferromagnetism, agree with experimental vals. obtained by Okamura. L. S. T.

**Change of thermal energy due to magnetisation in ferromagnetic substances.** T. OKAMURA (Sci. Rep. Tôhoku, 1936, **24**, 745—807).—The absorption and evolution of heat during magnetisation has been determined for Fe, Ni, Co, steel, K.S. magnet steel, Ni–Fe alloy, and single Fe crystals. Reversible (magneto-caloric) and irreversible (magnetic hysteresis) changes occur. In the initial magnetisation, starting from the magnetically neutral state, the curves of irreversible effect for all the ferromagnetics studied have the same form as the curve of magnetisation. The reversible heat curves, plotted against field, are similar for all but Co. In weak fields the heat is absorbed and absorption at first increases, reaches a max., decreases, and finally changes to heat evolution. For Co, absorption only is observed. In cyclic magnetisation, starting from max. fields, the irreversible effect does not appear until zero field is approached. On passing to the negative side heat evolution becomes marked and then approaches a saturation val. The irreversible heat effect is in satisfactory agreement with the val. calc. on the basis of the Honda–Ôkubo theory of ferromagnetic substances, and the reversible effect is that to be expected on thermodynamic grounds. M. S. B.

**Antiferromagnetic exchange problem at low temperature.** L. HULTHÈN (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 190—200).—Mathematical. O. J. W.

**Influence of the thermal variation of the molecular field on the Curie constant.** L. NÉEL (Compt. rend., 1936, **202**, 1038—1040; cf. A., 1935, 1063).—Theoretical. The Curie const. $C$ given by $C/\chi=T-\theta$, ($\theta$ is at. magnetic susceptibility, $T$ the abs. temp., and $\chi$ the Curie point) is corr. for the influence of the mol. field. For Ni and Co the new const. $C_0=0\cdot379$ and $0\cdot99$, respectively, corresponding with 1 and 2 uncompensated spins per atom and electron configurations $3d^94s$ and $3d^84s$. By analogy Fe should have 3 uncompensated spins and an electron configuration $3d^74s$, and should have a val. of $C_0=1\cdot862$; $C=1\cdot23$ and the val. of $C_0-C$ is considered reasonable when allowance is made for the mol. field.

R. S. B.

**Ferromagnetism of nickel.** J. C. SLATER (Physical Rev., 1936, [ii], **49**, 537—545).—By using metallic energy levels extrapolated from Cu to Ni, the energy difference between a non-magnetic and a ferromagnetic state with permanent magnetic moment is calc. for Ni; the ferromagnetic state is the stable one. Saturation magnetic moment and Curie point are calc. in agreement with experiment. N. M. B.

**Adhesion of two metallic surfaces in a vacuum, and the diminution of the adhesion in certain**

**gases.** R. Holm and B. Kirschstein (Wiss. Veröff. Siemens-Werken, 1936, 15, 122—127).—The adhesion of metallic surfaces was investigated in connexion with the formation of a surface film on the metals. The inclination of a wire when the substance (in the form of a cylinder threaded on the wire) would just slide down was determined for the contacts Ni–Ni, Pt–Pt, Ni–Pt, and graphite–Ni. In vac. and in inert gases ($N_2$ and A) the outgassed metals adhered so strongly that no sliding occurred even at an inclination of 90°, but for graphite–Ni, and in all cases in $O_2$, $H_2$, $H_2O$ vapour, and some org. vapours, sliding occurred, pointing to the existence, under these conditions, of a surface film on the metals. A. J. M.

**Quantum mechanical calculation of the elastic constants of univalent metals.** K. Fuchs (Proc. Roy. Soc., 1936, A, 153, 622—639).—The elastic consts. of Li, Na, K, and Cu have been calc. by means of an extension of the method used by Wigner and Seitz (A., 1933, 660) for calculating the lattice energy and compressibility of univalent metals. Good agreement with the observed vals. is obtained for Cu. As no experimental data exist for the alkalis, the Debye characteristic temp. are calc. for Li, Na, and K from the theoretical elastic consts., and compared with the vals. observed at low temp. The agreement is satisfactory. The Cauchy relations are not satisfied. L. L. B.

**New form of crystalline quartz at −183·5°.** H. Osterberg (Physical Rev., 1936, [ii], 49, 552—553).—Specially oriented Y cuts of quartz ceased abruptly to oscillate piezoelectrically near the b.p. of liquid air. The transformation to the new δ form was at −183·5°. The discontinuity in the optical rotatory power at the $\alpha \longleftrightarrow \delta$ transition was investigated; the changes were more abrupt at the $\alpha \rightarrow \delta$ than at the $\delta \rightarrow \alpha$ transition, but were much less rapid than the simultaneous piezoelectric changes. The $\delta \rightarrow \alpha$ transition temp. must be above −182·4°. N. M. B.

**Influence of mechanical deformation on the transformation velocity of polymorphic metals. II. The influence of metallic impurities.** E. Cohen and A. K. W. A. van Lieshout (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 352—358; cf. A., 1935, 688).—1% of Bi, Pb, Sb, Cd, and Ag decreases and 0·01—1% of Al and Zn greatly increases the speed of transformation of mechanically deformed Sn at −50°. The influence of Zn is a max. with 0·05% (also at 0°). The influence of 0·05% of Al and Zn has also been studied at 0°, −11°, and −22°. R. S. B.

**Localisation of the transition points of allotropic metals by means of the method of Saladin and Le Chatelier.** E. Rosenbohm and F. M. Jaeger (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 366—374).—When Ni is heated in a high vac. a transition $\alpha \rightleftharpoons \beta$ occurs sharply at 369—370°. On cooling, the transition temp. ($T$) is 6° < before, and this difference increases with the speed of cooling. In presence of 50—60 mm. of $H_2$ $T = 363$—364° on heating and cooling, and at 2—60 mm. the change in $T$ from the val. in a vac. is independent of pressure. Discrepancies in the literature in the vals. for $T$ are probably due to adsorbed gases. With $AuSb_2$ transitions occur at 355° and 404°. The second, $\beta \rightleftharpoons \alpha$, occurs much more slowly and, unlike the first, $\beta \rightleftharpoons \gamma$, shows hysteresis on cooling. With the $\beta \rightleftharpoons \gamma$ the temp. coeff. of $c_p$ is the same for both forms. R. S. B.

**Polar isomorphism.** A. E. Fersman (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 119—122).—A discussion. Hahn's law is restated as follows: the ions of the elements are caught in another crystal lattice from dispersed solutions only if their size and type allow them to form with this lattice an isomorphous structure, and if this structure is more advantageous, as regards energy, than the pure crystal. H. J. E.

**Electrical conductivity of transition metals.** N. F. Mott (Proc. Roy. Soc., 1936, A, 153, 699—717; cf. A., 1935, 1063).—Mathematical. A formal theory of conductivity for metals, such as the transition metals, where the conduction electrons occupy two Brillouin zones, is developed. Certain anomalies in the resistance–temp. curves of the paramagnetic metals Pd, Pt, and Ta are explained. The resistance of ferromagnetic metals is discussed, and an expression obtained for the decrease of the resistance of Ni in a magnetic field. It is shown qualitatively why the alloy Cu–Ni has zero temp. coeff. at room temp. L. L. B.

**Measurement of the electrical resistance of metals as function of the temperature by means of a twin galvanometer with photographic recording.** E. Rosenbohm and F. M. Jaeger (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 374—383).—The increments in electrical resistance ($R$) per 10° for Ni in a vac. increase regularly up to 358° and then rapidly decrease to a const. val. at 380°. At 350—365° an inflexion occurs in the $R$–$T$ curve, perhaps associated with the change $\alpha \rightarrow \alpha'$ (hexagonal). In presence of 60 mm. of $H_2$ $R$ is > for the pure metal, but the temp. coeff. is unchanged up to 345°, when $H_2$ begins to be released from the metal. At 345—375° there is indication of the formation of the $\alpha'$ phase. R. S. B.

**Diamagnetic susceptibility of heavy water.** F. E. Hoare (Nature, 1936, 137, 497—498).—The val. obtained by Gouy's method for 99·2% $D_2O$ is $0{\cdot}648 \pm 0{\cdot}001 \times 10^{-6}$ unit at 20°, corresponding with a mol. susceptibility of 12·96. L. S. T.

**Magnetic susceptibility of disubstituted benzene derivatives.** K. Kido (Sci. Rep. Tôhoku, 1936, 24, 701—706).—31 derivatives have been examined and most of the results are in satisfactory agreement with calc. vals. The mol. susceptibility of *p*-derivatives is generally < that of the corresponding *o*-derivatives. M. S. B.

**Magnetic properties and structure of the hæmochromogens and related substances.**—See this vol., 616.

**Diffraction of light by ultrasonic waves.** R. Lucas (Compt. rend., 1936, 202, 1165—1166).—An apparatus for testing the validity of the different theories relative to the diffraction of light by ultrasonic waves is described. M. S. B.

**Diffraction of light by progressive ultrasonic waves.** E. Hiedemann and E. Schreuer (Z. Physik, 1936, **99**, 363—368).—An extension of Raman and Nath's theory (cf. this vol., 148) to cover frequency changes and an ultrasonic field of finite width. A. B. D. C.

**Diffraction of light by ultrasonic waves.** S. M. Ritov (Physikal. Z. Sovietunion, 1936, **8**, 626—643).—The theory of Debye and Brillouin is extended, the case of small angle of incidence being treated. To test the results, a goniometer was used to investigate the diffraction with ultrasonic waves in liquids ($C_6H_6$ and PhMe) and in quartz. There is satisfactory agreement. A. J. M.

**Ultrasonic velocities in some organic liquids. II.** S. Parthasarathy (Proc. Indian Acad. Sci., 1936, **3**, **A**, 285—289).—Data are recorded for ultrasonic velocities and adiabatic compressibilities of a no. of di-esters, *o*-, *m*-, and *p*-xylene, quinoline, and *o*-toluidine, for $7 \cdot 37 \times 10^6$ cycles per sec. and room temp. L. J. J.

**Heat capacities of quartz, cristobalite, and tridymite at low temperatures.** C. T. Anderson (J. Amer. Chem. Soc., 1936, **58**, 568—570).—Data are recorded for the range 50—300° abs. The corresponding entropies are 10·06, 10·34, and 10·50, respectively. E. S. H.

**Heat capacities of vanadium, vanadium trioxide, vanadium tetroxide, and vanadium pentoxide at low temperatures.** C. T. Anderson (J. Amer. Chem. Soc., 1936, **58**, 564—566).—Data are recorded for the range 55—300° abs. The corresponding entropies have been calc. E. S. H.

**Heat capacity of lead sulphate at low temperatures.** C. T. Anderson (J. Amer. Chem. Soc., 1936, **58**, 567).—Data are recorded for 55—300° abs. The calc. entropy is 35·2. E. S. H.

**Limiting high-temperature rotational partition function of non-rigid molecules. I. General theory. II. $CH_4$, $C_2H_6$, $C_3H_8$, $CHMe_3$, $CMe_4$, and *n*-butane. III. Benzene and its eleven methyl derivatives.** L. S. Kassel (J. Chem. Physics, 1936, **4**, 276—282).—The theory of Eidinoff and Aston (A., 1935, 1064) is developed and applied to the calculation of mol. entropies, giving results in agreement with third-law data. L. J. J.

**Heat of evaporation of heavy hydrogen.** K. Clusius and E. Bartholomé (Nachr. Ges. Wiss. Göttingen, 1935, [ii], **1**, 49—58; Chem. Zentr., 1935, ii, 961—962).—The latent heat of evaporation $L$ of $D_2$ (cf. A., 1935, 155) at 19·6° abs. has been directly measured in a liquid-$H_2$ calorimeter. $L$, corr. to the ideal gas state by means of the equation of state for $H_2$, is 304·7 g.-cal. per mol. $L_0$ at 0° abs. is calc. as 274·0 g.-cal., giving a measured difference of 90·6 g.-cal. in zero-point energy between $H_2$ and $D_2$. The entropy $S_{\text{therm.}}$ of $D_2$ at 298·1° abs.=33·927; total entropy=39·02 in agreement with the calc. val. The following Trouton's consts. at low temp. are recorded: He 4·8, $H_2$ 10·6, $D_2$ 12·9, Ne 14·9. J. S. A.

**Variations of the physical properties of some liquids in the neighbourhood of the m.p.** A. Banchetti (Gazzetta, 1936, **66**, 65—71).—The rate of cooling of anethole does not show any sudden change at the m.p. when the liquid is cooled slowly and remains supercooled (cf. A., 1900, ii, 465). O. J. W.

**Melting curve of a compound partly dissociated into its components.** J. J. van Laar (Physica, 1936, **3**, 255—256).—A claim of priority (cf. Mlodziejowski, A., 1935, 582). L. J. J.

**Preliminary experiments on temperature equilibria at very low temperatures.** N. Kürti, B. V. Rollin, and F. Simon (Physica, 1936, **3**, 266—274).—The rate of establishment of temp. equilibrium at temp. obtained by the magnetic method has been examined. Equilibrium between $Fe^{III}$ $NH_4$ alum (I) and liquid He at 0·2° abs. is attained in 30 sec., so that the time-const. for the equilibrium spin system-lattice is < this. The thermal conductivities of (I) and $Cr^{III}$ K alum between 0·07° and 0·16° abs. are $\sim 10^{-5}$ c.g.s.; hence attainment of equilibrium within the salt is slow. L. J. J.

**Universal expression for the limits of physicochemical relations.** G. A. Korsheniovski (J. Phys. Chem. U.S.S.R., 1934, **5**, 1321—1331).—Theoretical. Ch. Abs. (*e*)

**Quantum statistics of melting.** L. Tarschisch (Z. Physik, 1936, **99**, 259—273).—A theory of melting is deduced from Debye's theory of sp. heats and Born's dynamics of crystals, using the Fermi–Debye statistics. A. B. D. C.

**Liquid densities of propylene and methyl ethyl ether as determined by a modified dilatometer method.** D. B. Pall and O. Maass (Canad. J. Res., 1936, **14**, **B**, 96—104).—An improved dilatometric apparatus is described and with it the *d* of $C_3H_6$ and MeOEt have been determined from 20° to 80° and 70° to 120°, respectively. The law of corresponding states is obeyed to within < 0·96° of the crit. temp. R. S.

**Vapour pressures of the xylenes and mesitylene.** L. S. Kassel (J. Amer. Chem. Soc., 1936, **58**, 670—671).—For *o*-xylene (0—80°) $\log_{10} P = -2830 \cdot 0/T - 5 \log_{10} T + 22 \cdot 7480$; *m*-xylene (0—80°) $-2876 \cdot 3/T - 5 \log_{10} T + 22 \cdot 9424$; *p*-xylene (0—80°) $-2930 \cdot 0/T - 5 \log_{10} T + 23 \cdot 1000$; mesitylene (0—100°) $-3104 \cdot 5/T - 5 \log_{10} T + 23 \cdot 1929$. The calc. entropies of vaporisation to a perfect gas at 25° and 1 atm. are 24·35, 25·24, 25·96, and 26·39 e.u., respectively. E. S. H.

**Calculation of van der Waals *a* and *b*.** J. E. Verschaffelt (Wis. nat. Tijdschr., 1935, **7**, 149—154; Chem. Zentr., 1935, ii, 1143).—A crit. review. J. S. A.

**General constant of van der Waals.** R. Lautié (Compt. rend., 1936, **202**, 1059—1061).—Theoretical. The van der Waals const. $a$, defined by $\log P_c/P = a_1\{(T_c/T) - 1\}$, where $P_c$ and $T_c$ are the crit. pressure and temp., is replaced by $a_2 = \lambda/[4 \cdot 571 T_c(1 - 1/P_c)]$, where $\lambda$ is the mol. latent heat of vaporisation at the b.p. ($T_1$). The agreement between $a_1$ and $a_2$ is good even for "abnormal" liquids, for which $a_1 < 2 \cdot 8$

or $> 3{\cdot}2$. With sufficient accuracy $\lambda=4{\cdot}3a_2T_c$. The empirical relation $\lambda/T_c=3{\cdot}589 \log T_c+1{\cdot}13+0{\cdot}00559T_c$ has also been derived, and using this and writing $T_c/T_1=3/2$ a third const. $a_3$, agreeing sufficiently well with $a_1$ and $a_2$, is deduced. $a_3=0{\cdot}7621\times\log T_1+0{\cdot}5822+0{\cdot}001322T_1$. R. S. B.

**Thermodynamic equilibrium in the gravitational field.** F. O. Koenig (J. Physical Chem., 1936, **40**, 373—378).—Mathematical. F. L. U.

**Variation in volume of heavy water on freezing.** J. Timmermans, M. Hennaut-Roland, and D. Rozental (Compt. rend., 1936, **202**, 1061—1063; cf. A., 1935, 815).—Vals. of $d$ for pure $D_2O$ have been determined. $d^{4\cdot3}=1{\cdot}10573$, $d^{11\cdot6}=1{\cdot}10621$, $d^{20}=1{\cdot}10556$, giving by extrapolation $d^{3\cdot82}=1{\cdot}1057$, and sp. vol. at $3{\cdot}82°=0{\cdot}9044$. For the solid $d^0=1{\cdot}01475$, and $d^5$ for $H_2O=0{\cdot}9159$. The sp. vols. of solid and liquid $D_2O$ at approx. 0° differ by 0·0811, which agrees sufficiently with published vals.; $dT/dp$ as calc. using the Clausius–Clapeyron equation also agrees with published vals. and is approx. the same for $D_2O$ and $H_2O$, viz., 0·00705° per kg. per sq. cm. R. S. B.

**Thermal expansion of water.** I. V. Ipatov (J. Phys. Chem. U.S.S.R., 1934, **5**, 1230—1231).—Experimental vals. (0—100°) are expressed by equations. Ch. Abs. (*e*)

**Thermal expansion of solids at low temperatures (Cu, Ni, Fe, zinc blende, LiF, calcite, aragonite, $NH_4Cl$).** H. Adenstedt (Ann. Physik, 1936, [v], **26**, 69—96).—The thermal expansion was investigated over the range 0° to −195° by an interference method. A metal thermostat operating between these temp. is described. The coeff. of expansion (α) of Cu, Ni, and Fe over this range agrees with vals. obtained from the formula of Grüneisen for regular monat. substances. The anomalies recorded by Simon *et al.* (A., 1930, 986) were not observed. Zn blende was investigated down to −253°, and gives at the lower temp. a negative val. for $\beta[=(1/l_0)(\delta l/\beta T)]$. For LiF, α agrees with the Grüneisen formula except at the lower temp. With falling temp. α for aragonite approaches the val. for a monat. solid, but calcite shows a negative vol. expansion at −172°. In the case of $NH_4Cl$ the transition point at −31° was verified. The behaviour of β for $NH_4Cl$ indicates that the transition is homogeneous. A. J. M.

**Negative expansion coefficient of silver iodide.** E. Cohen and H. L. Bredée (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 358—360).—The val. for the expansion coeff. of AgI determined by Jones and Jelen (cf. this vol., 279) is considered to be in error, since these authors used a mixture of α- and β-AgI, and $\beta \rightarrow \alpha$ during the experiment. Pure α-AgI has the coeff. found by Fizeau, viz., $-4{\cdot}1\times10^{-6}$ at 40°. R. S. B.

**Viscosity of gaseous oxygen at low temperatures; effect of pressure.** A. van Itterbeek and (Mlle.) A. Claes (Physica, 1936, **3**, 275—281).—Data obtained by the oscillating-disc method are recorded for 293·8°, 90·1°, 79·8°, and 72·0° abs., and $10^{-5}$—760 mm. pressure. η is independent of pressure down to about 5 mm. The calc. ratios of the mean mol. velocities at the temp. studied agree with the Maxwell–Boltzmann distribution. L. J. J.

**New comparison of the viscosity of $D_2O$ with that of $H_2O$.** W. N. Baker (J. Chem. Physics, 1936, **4**, 294—295).—Between 5° and 35°, η for $D_2O$ is approx. equal to η for $H_2O$ at a temp. 8·5° lower. L. J. J.

**Viscosity of liquid metals.** D. V. Colgate (J. Univ. Bombay, 1935, **4**, Part II, 83—85).—Formulæ are derived relating the viscosity of a monat. liquid with (*a*) the at. wt., m.p., and at. vol. at the m.p., and (*b*) with *d*, the at. wt., the Debye characteristic temp., and a const. dependent on the cryst. structure of the metal. The calc. vals. are in fair accord with experiment for Cd, Hg, Cu, Sn, and Pb. J. W. S.

**Diffusion isotherms for binary mixtures.** H. Lemonde (Compt. rend., 1936, **202**, 468—470).—Diffusion coeffs. (*D*) have been determined for the following mixtures: $H_2O$ with MeOH, EtOH, PrOH, $Pr^{\beta}OH$; $CHCl_3$ with $Et_2O$, $COMe_2$, EtOH; $C_6H_6$ with $CHCl_3$, MeOH, EtOH, $C_6H_{14}$; PhMe with EtOH. $D\times$viscosity (η) is const. only for very dil. solutions. In general the $D\eta$ curves show a max. or min. or both, the deviations apparently depending on the tendency to association. *D*–composition curves for homologous compounds in the same solvent have the same form. In dil. solution $D \propto$ vol. concn. F. L. U.

**Viscosities of aqueous solutions of nitric acid at low temperatures.** D. Schofield (Bol. Soc. Quim. Peru, 1935, **1**, 7—25).—At −17°, the fluidity–concn. curve shows max. deviation from the ideal mixture curve at $HNO_3,H_2O$. A thermostat suitable for temp. below 0° is described. L. A. O'N.

**Viscosity and conductivity in the system: fused KCl–LiCl.** S. V. Karpatschev, A. G. Stromberg, and V. N. Podtschainova (J. Gen. Chem. Russ., 1935, **5**, 1517—1526).—Conductivity and viscosity data for the range 400—900° indicate that Stokes' law is not applicable to the system. R. T.

**Thermal conductivity of liquids. Binary mixtures of water and glycerol.** O. K. Bates (Ind. Eng. Chem., 1936, **28**, 494—498).—In a modification of the apparatus previously employed (B., 1933, 415) thermal conductivity measurements have been made for a complete range of mixtures of $H_2O$ and glycerol (I) at 10—80°. The coeff. of thermal conductivity of pure (I) is independent of temp. over the range considered. M. S. B.

**Vaporisation equilibria in the binary salt mixture $HgCl_2$–$HgBr_2$, and in the reciprocal salt-pair (Na, K) (Cl, Br).** H. Hintz and K. Jellinek (Z. Elektrochem., 1936, **42**, 187—200; cf. A., 1933, 770).—Comparison of the total v.p. of liquid $HgCl_2$–$HgBr_2$ mixtures with the partial pressures of the components, measured at 238°, indicates that the liquid behaves as an ideal mixture, that no compound is formed, and that only single mols. are present. Similar measurements at 1250° for the mixtures NaCl–KCl, NaBr–KBr, NaCl–NaBr, and KCl–KBr lead to the same conclusions with regard to these mixtures. A diagram of the vapour equilibria of the reciprocal salt-pair NaCl–KBr is given. F. L. U.

**Vapour pressure of the binary system, $PbCl_2$–AgCl.** D. N. Tarasenkov and A. V. Bogoslovskaja (J. Gen. Chem. Russ., 1935, 5, 1687—1689).—V.-p. data are recorded for the interval 500—800°. It is concluded that $PbCl_2$ may be separated from AgCl by distillation at 700—800°. R. T.

**Heat of vaporisation in the system carbon disulphide–methyl alcohol.** S. I. Tscherbov (J. Gen. Chem. Russ., 1935, 5, 1645—1651).—Vrevski's equation connecting the latent heat of vaporisation of a liquid mixture with those of its components, the composition of the vapour phase, and the differential heat of dilution of the components (A., 1930, 404) is shown to hold for the system $CS_2$–MeOH at 20°. R. T.

**Phase equilibria in hydrocarbon systems. XII. Specific heats of some mixtures of propane, *n*-butane, and *n*-pentane.** B. H. Sage, H. S. Backhus, and T. Vermeulen (Ind. Eng. Chem., 1936, **28**, 489—493).—Sp. heats at const. pressure have been determined for binary mixtures of $C_3H_8$, $n\text{-}C_4H_{10}$, and $n\text{-}C_5H_{12}$ at 21—104° in the condensed liquid phase. The mixtures follow closely the laws of ideal solutions as was indicated by determining pressure–vol.–temp. relations for $C_3H_8$–$n\text{-}C_5H_{12}$ mixtures and calculating heat content and entropy. M. S. B.

**Diffusion and azeotropism in binary mixtures.** H. Lemonde (Compt. rend., 1936, **202**, 1069—1071; cf. this vol., 674).—The diffusion coeff. (*D*) increases or decreases with concn. in a binary mixture according as the v.p. decreases or increases, provided that the v.p. departs sufficiently from the linear law. Mixtures may be classified in terms of the function $D\eta$ which seems to be very sensitive to variations in the magnitude of the intermol. forces. R. S. B.

**Orthobaric azeotropes. Esters–halides.** M. Lecat (Ann. Soc. Sci. Bruxelles, 1936, **56**, **B**, 41—54; cf. this vol., 280).—Data are given for 434 binary systems formed by 80 esters and 63 halogenated hydrocarbons. These include 148 cases of azeotropism (23 negative). M. S. B.

**Solubility in liquids of gas mixtures under pressure. II. Thermodynamical calculation of solubility in water of a mixture of nitrogen and hydrogen under pressure.** I. R. Kritschevski and J. S. Kasarnovski (Z. physikal. Chem., 1936, **176**, 48—54; cf. this vol., 29, 30).—Assuming that a 1 : 3 mixture of $N_2$ and $H_2$ is equiv. to an infinitely dil. solution of $N_2$ in $H_2$, the partial mol. vols. and fugacities of $N_2$ in a mixture containing 76·42% $H_2$ and the solubility in $H_2O$ of $H_2$ and $N_2$ from this mixture have been calc. for pressures of 50—1000 atm. at 25°. The results agree with published experimental data. R. C.

**Solubility of lanthanum in mercury from 0° to 50°.** W. G. Parks and J. L. Campanella (J. Physical Chem., 1936, **40**, 333—341).—The solubility of La in Hg between 0° and 50° is low, and is given by: $\log N = -1020/T - 0{\cdot}4575$ ($N$=at. fraction of La, $T$=abs. temp.). La amalgam is considered unsuitable for precise e.m.f. measurements. F. L. U.

**Solubility of lead bromate and its activity coefficients in solutions of electrolytes.** F. H. MacDougall and E. J. Hoffman (J. Physical Chem., 1936, **40**, 317—331; cf. A., 1930, 699).—The solubility of $Pb(BrO_3)_2$ in $H_2O$, and in presence of nitrates of K, Na, Li, Ca, Sr, and Pb, has been determined at 25°. The theory of Debye and Hückel is not valid for these solutions if complete ionisation is assumed. Activity coeffs. are calc. assuming the stages: (1) $Pb(BrO_3)_2 \rightleftharpoons PbBrO_3^{\cdot} + BrO_3'$; (2) $PbBrO_3^{\cdot} \rightleftharpoons Pb^{\cdot\cdot} + BrO_3'$. F. L. U.

**Solubility of lead sulphate in aqueous sulphuric acid at high concentrations.** H. D. Crockford and J. A. Addlestone (J. Physical Chem., 1936, **40**, 303—305; cf. A., 1935, 159).—Solubilities of $PbSO_4$ at 0°, 25°, 35°, and 50° are given for $[H_2SO_4] > 80\%$. At 0° $H_2SO_4$ and $H_2SO_4,H_2O$ may exist as solids. At the higher temp. the only solid phase is $PbSO_4$. The $PbSO_4$–$H_2SO_4$ eutectic is at 5·4°. F. L. U.

**Solubility in water and aqueous sodium chloride of α-naphthylaminemonosulphonic acids and their sodium salts.** P. I. Sokolov (Anilinokras. Prom., 1935, 5, 149—153).—Solubility data are recorded for α-naphthylamine-2-, -4-, -5-, -6-, -7-, and -8-sulphonic acids and their Na salts at 25°. R. T.

**Influence of degree of dispersion on physicochemical constants. VI.** E. Cohen and J. J. A. Blekkingh (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 154—163; cf. this vol., 20).—The solubility of salicylic acid at 25° has been studied under various conditions. The previously recorded high and discrepant vals. are attributed to the high degree of dispersion of the solid phase and to the presence of about 0·2% of $p\text{-}OH\cdot C_6H_4\cdot CO_2H$. O. J. W.

**Solidification diagram of copper–zinc alloys.** W. Broniewski, J. T. Jablonski, and S. Maj (Compt. rend., 1936, **202**, 411—414).—The m.-p. diagram of Cu–Zn alloys indicates the presence of the compounds CuZn, $CuZn_2$, and $CuZn_6$. CuZn and $CuZn_6$ show allotropic changes at about 460° and 600°, respectively. J. W. S.

**Study of copper–tin alloys by *X*-ray analysis.** E. A. Owen and E. Williams (J. Inst. Metals, 1936, **58**, Advance copy, 153—167).—The δ-phase in Cu–Sn alloys is a solid solution with a range varying from zero at the eutectoid point (67·45% Cu, 330°) to 0·48% at 550°. The η-phase is also a solid solution extending from 61·68 to 62·10% at 250° and from 61·68 to 62·20% Cu at 530°. Below 330° δ decomposes into α+η. A. R. P.

**Orientation in peritectic structures.** A. B. Greninger (Nature, 1936, **137**, 657—658).—*X*-Ray investigation of the reaction α+liquid → β in the Cu–Zn system shows that the orientations assumed by the β-phase are definitely related to the orientation of the α-phase. Seeding the crystallisation of a pure β-alloy (52% Cu) with a Cu single crystal gives the sequence Cu crystal seed, primary cryst. α-phase having the same orientation as the Cu seed, large β-grains having a narrow rim of segregated α-phase and originating in the peritectic reaction α+liquid → β. L. S. T.

**Electrical conductivity and equilibrium diagram for binary alloys. XIX. System sodium–thallium.** G. Grube and A. Schmidt (Z. Elektrochem., 1936, 42, 201—209; cf. this vol., 151).—In addition to NaTl and $NaTl_2$, the existence of *compounds* $Na_2Tl$ and $Na_6Tl$ is established by thermal analysis and conductivity measurements. Solid solutions occur over a wide range in systems rich in Tl. NaTl melts without decomp. at 305°, whilst the other compounds are formed as a result of solid reactions. Alloys with Na 17—24 at.-%, after quenching from 200°, undergo considerable hardening at room temp. F. L. U.

**Constitution of tin-rich antimony–tin alloys.** D. Hanson and W. T. Pell-Walpole (J. Inst. Metals, 1936, 58, Advance copy, 79—90).—The system up to 14% Sb has been examined by thermal analysis, micrographically, and by the electrical resistance method. The liquidus consists of two branches, the first corresponding with the separation of the α-Sn solid solution and the second with the separation of cuboid-δ; at 246° a peritectic reaction occurs between δ and liquid (9% Sb) to form α (10·5% Sb). The solubility of Sb in Sn decreases from 10·5% at 246° to 4% at 190° and to 3·5% at 100°. Characteristic microstructures are illustrated. A. R. P.

**Over-structure phenomena in nickel–arsenic alloys.** F. Laves (Fortschr. Min., 1935, 19, 33—37; Chem. Zentr., 1935, ii, 972—973).—Rotation photographs obtained with tetragonal $Ni_3As_2$ (maucherite) give *a* 3·45, *c* 21·7 A., with a superposed two-dimensional overstructure having *a* 6·9 A. J. S. A.

**Mixed crystal problem.** H. O'Daniel (Fortschr. Min., 1935, 19, 48—52; Chem. Zentr., 1935, ii, 1126).—The possible ratios of mixed crystal components which permit the development of a perfect overstructure are discussed. J. S. A.

**New method of separation of radium by rapid reduction in barium content.** (Mme.) B. E. Marques (J. Chim. phys., 1936, 33, 306—316).—Previous experimental evidence (this vol., 421) indicates that, by slow evaporation at 20° of saturated aq. $BaBr_2$ containing Ra, until about 60% of the $BaBr_2$ has crystallised out, practically the whole of the $RaBr_2$ present may be conc. in the $BaBr_2$ crystals. By successive dissolution and partial recrystallisation a product rich in Ra may be obtained with comparatively little loss. M. S. B.

**Radon hydrate.** B. A. Nikitin (Z. anorg. Chem., 1936, 227, 81—93).—Rn left in contact with snow at −3·5° remains entirely in the gas phase, but if $SO_2$ is introduced into the latter, the Rn is transferred to the solid phase $SO_2,6H_2O$. The distribution of Rn between the gaseous and solid phases has been measured, for different relative amounts of the phases, and when equilibrium is reached, both from $SO_2$+Rn in contact with snow and from Rn in contact with preformed $SO_2,6H_2O$. Under these conditions the partition factor $D=[Rn]_{cryst}/[Rn]_{gas}-[SO_2]_{gas}/[SO_2]_{cryst}$ is const. =0·57. Similar experiments with $H_2S,6H_2O$ give $D=2·4$. The results afford conclusive evidence of the existence of $Rn,6H_2O$ isomorphous with the hexahydrates of $SO_2$ and $H_2S$, and occupying an intermediate position with regard to stability. All experiments were carried out at −3·5°, below the eutectic temp. of $H_2O$ and the respective hydrates. F. L. U.

**Adsorption of nitrogen on tungsten.** J. K. Roberts (Nature, 1936, 137, 659—660).—Amounts of $N_2$ insufficient to cover a W wire are rapidly and completely adsorbed, leaving a negligible residual pressure. $N_2$ thus resembles $H_2$ (cf. this vol., 282). L. S. T.

**Diffusion of hydrogen through copper.** E. O. Braaten and G. F. Clark (Proc. Roy. Soc., 1936, A, 153, 504—512).—The rate of diffusion of $H_2$ through Cu has been determined for several temp. and pressures. The rate varies with the pressure in a manner consistent with the equation of Smithells and Ransley (A., 1935, 692); the adsorption factor causes a slight departure from the equation at about 2 mm. The effect of temp. is given by the usual exponential relation. L. L. B.

**Adsorption of radon by glass.** S. C. Lind and R. Livingston (J. Physical Chem., 1936, 40, 419—420; cf. A., 1933, 564).—Rn in Pyrex glass bulbs undergoes slow irreversible adsorption on the walls, amounting to 16% in 68 hr. The need for taking account of this effect in quant. work is emphasised. F. L. U.

**Pre-Gibbs adsorption by surface rearrangement.** J. W. McBain (Nature, 1936, 137, 659).—The possible existence of a preliminary factor contributing to the lowering of $\eta$, viz., an interchange of positions between mols. of solute and solvent within a few mol. diameters of the surface, is discussed in relation to the low vals. of $\eta$ shown by soap solutions. L. S. T.

**Method of studying conditions within diffusion layers.** T. Teorell (J. Biol. Chem., 1936, 113, 735—748).—An apparatus is described for measuring diffusion gradients by the use of a no. of membranes in series separated by well-stirred solutions so that the diffusion gradients occur exclusively in the membranes. Analysis of the solutions in the chambers bounded by these membranes permits the plotting of these gradients. H. D.

**Sorption of iodine by polyvinyl alcohol.** W. Gallay (Canad. J. Res., 1936, 14, B, 105—113).—The adsorption isotherms of I on polyvinyl alcohol polymerides pptd. by NaCl and by $MgSO_4$ have been studied. When MeOH and EtOH are the pptg. agents, the adsorption follows the simple distribution law. Adsorption of $NaHCO_3$ on the NaCl-pptd. alcohol is also linear, but the I adsorption is not affected by pretreatment with electrolytes. It is suggested that a certain colloidal size and a certain type of linking are necessary for the formation of blue I compounds. R. S.

**Adsorption of proteins. Influence of hydrogen-ion concentration on the adsorption of hæmoglobin by kaolin.** M. Paić and (Mlle.) V.

Deutsch (Compt. rend., 1936, **202**, 1283—1285).—The adsorption isotherms in presence of various buffer solutions show a discontinuity at low concns. With varying $p_H$, the adsorption passes through a max., the position of which depends on the buffer concn.
L. J. J.

**Inner adsorption in salt crystals. III. Nature of inclusion of ZnS in CuS.** D. Balarev (Z. anal. Chem., 1935, **102**, 408—411; cf. A., 1927, 925).—Polemical against Kolthoff (A., 1932, 481). The ease with which ZnS, copptd. with CuS, is extracted by HCl is held to point to its true inner adsorption in the CuS lattice.
J. S. A.

**Coprecipitation and after-precipitation. Ageing of precipitates.** I. M. Kolthoff (Z. anal. Chem., 1936, **104**, 321—333).—Polemical against Balarev (preceding abstract). The author's views are summarised.
J. S. A.

**Gas-solid equilibria. VI. Adsorption from binary gas mixtures by silica gel.** B. Lambert and H. S. Heaven (Proc. Roy. Soc., 1936, **A**, **153**, 584—600).—The pressure–concn. equilibria at 0° between $SiO_2$ gel and $O_2$–A, $O_2$–$N_2$, and $O_2$–He mixtures (containing equal proportions of the two gases in each case) have been investigated. A procedure is described by means of which it is possible to determine the vols. of the two gases *X* and *Y* adsorbed and the partial pressures of *X* and *Y* in the equilibrium gaseous phase: (*a*) when either *X* or *Y* is given priority of contact with the solid adsorbent; and (*b*) when *X* and *Y* in equal concns. reach the adsorbent simultaneously. With $O_2$–A mixtures, when the $O_2$ is given priority of contact, the adsorbed phase at equilibrium contains 3 times as much $O_2$ as A; when A is given priority of contact, the adsorbed phase contains half as much $O_2$ as A; and when the two gases reach the gel simultaneously, equal amounts of $O_2$ and A are found in the adsorbed phase. A theory of adsorption is suggested, involving the assumption of an adsorbed phase consisting of two layers of gas mols. With $O_2$–$N_2$ mixtures, $O_2$ is adsorbed more, and $N_2$ less, than each would be in the absence of the other. With $O_2$–He mixtures, $O_2$ is adsorbed as it would be in the absence of He, provided that the gel has previously been thoroughly "washed out" with $O_2$. The adsorptive power for He at 0° is negligible.
L. L. B.

**Active oxides. XCIV. Sorptive capacity of goethite during dehydration.** J. Hampel (Z. Elektrochem., 1936, **42**, 185—187).—From expts. with Congo-red, acid fuchsin, and eosin in MeOH solution the relation between the sorptive capacity of artificially prepared goethite in various stages of dehydration and the ratio $H_2O/Fe_2O_3$ has been determined and is interpreted in accordance with conclusions previously reached (A., 1935, 1204; this vol., 441).
F. L. U.

**Solution state of film-forming substances.** J. Scheiber and O. Baier (Kolloid-Beih., 1936, **43**, 363—416).—The viscosity of solutions of many resins, highly-polymerised substances, such as rubber and its derivatives, and cellulose nitrate in a large no. of org. solvents has been determined. The effects of changing and mixing the solvents are discussed for the several systems, but wider generalisations have not been deduced.
E. S. H.

**Wettability of quartz, calcite, and gypsum by molten sulphur.** K. N. Samochvalov and N. A. Held (Kolloid-Z., 1936, **75**, 89—74).—Wetting by S at 120° and 140° in $H_2O$, air, and $H_2O$ vapour has been investigated by autoclave procedure. Addition of $Na_2CO_3$, $Na_2SiO_3$, or oak-bark extract reduces the wettability of $CaSO_4,0{\cdot}5H_2O$ or $CaCO_3$ by S, and of $SiO_2$ by bituminous S.
E. S. H.

**Laminar systems. III. Formation of thin layers of bismuth and lead sulphides on the surface of bismuth and lead salt solutions.** S. G. Mokruschin, R. B. Ginsburg, and N. M. Demjanova (Kolloid-Z., 1936, **75**, 10—14; cf. A., 1935, 1317).—The prep. of films of $Bi_2S_3$ or PbS, with a max. thickness of 1500—2000 A., on the surface of aq. $Bi(NO_3)_3$ or $Pb(OAc)_2$ by the action of $H_2S$ is described.
E. S. H.

**Mechanical resistance of the skin of alumina and its influence on the surface tension of the fused metal.** A. Portevin and P. Bastien (Compt. rend., 1936, **202**, 1072—1074).—The mechanical resistance of the skin of $Al_2O_3$ formed on Al by heating for approx. 1 min. at 700° is 1960 dynes per cm. The thickness of the film is $10^{-5}$ cm., giving a tensile strength of 2 kg. per sq. mm., which is much > that for cryst. $Al_2O_3$. The surface tension of Al fused in air is 840 dynes per cm., but for Al fused in A it is 300 dynes per cm.
R. S. B.

**Surface activity and absorption of amino-acids. V. Diamino-acids. VI. Position isomerides of monoamino-acids.** T. Ito (J. Agric. Chem. Soc. Japan, 1936, **12**, 204—207, 208—215).—V. Histidine (I), lysine (II), and arginine (III), over the range $p_H$ 1—13, have very little influence on the $\gamma$ of $H_2O$; both neutral mols. and ions are surface inactive. The max. adsorption of (I) on charcoal occurs at $p_H$ 7·5, whilst for (II) and (III) the max. are at $p_H$ 9·5. The order of adsorption for (II) and (III) is neutral mol.$\nless$anion$>$cation, and for (I) neutral mol.$>$anion$=$cation.

VI. The reduction of $\gamma$ by various $NH_2$-acids follows the order $\alpha$-aminohexoic$>$$\alpha$-aminovaleric$>$ $\epsilon$-aminohexoic$>$$\gamma$-aminovaleric$>$$\delta$-aminovaleric acid (IV). On charcoal the cations are adsorbed as strongly as the neutral mols. but the anions are less readily adsorbed. In the case of (IV) the adsorption of the cation is > that of the neutral mol.
J. N. A.

**Surface tension of systems containing a tautomeric substance.** R. V. Mertzlin (J. Phys. Chem. U.S.S.R., 1934, **5**, 1210—1214).—Surface tension measurements for the system $PhNO_2$–*o*-$OH{\cdot}C_6H_4{\cdot}NO_2$ at 20—130° show the existence of two tautomeric forms of the latter. The surface tension isotherms are convex. to the concn. axis at temp. above, and concave below, the region of tautomeric change.
Ch. Abs. (*e*)

**Influence of denaturation on spreading of proteins on a water surface.** H. Neurath (J. Physical Chem., 1936, **40**, 361—368).—Pressure-area relations for films of ovalbumin (I) and serum-albumin (II) on $H_2O$ have been determined. Spreading is greater at the isoelectric point ($p_H$ 4·8) than at $p_H$ 4·4. (II) spreads to an area (1·05 sq. m. per mg.) 15% $>$ for (I). Previous denaturation by heat completely prevents, and irradiation with ultra-violet light partly inhibits, spreading. Fully spread films can be caused to collapse by irradiation. An explanation of the observations is given. F. L. U.

**Formation of Liesegang rings in presence of precipitates.** B. N. Sen (J. Physical Chem., 1936, **40**, 369—372).—The formation of Liesegang rings of Prussian-blue by diffusion of aq. $K_4Fe(CN)_6$ into magmas of $CaSO_4$ or $BaSO_4$ and aq. $FeCl_3$ has been studied. F. L. U.

**Dependence on temperature of the apparent molecular volume of dissolved electrolytes. I.** B. Pesce (Gazzetta, 1936, **66**, 99—104).—Measurements of *d* for KCl and NaCl solutions of varying concn. at 0·06°, 25°, 45°, 65°, and 85° are recorded. The apparent mol. vol. of both salts is a max. at 65°. O. J. W.

**Measurement of coefficient of diffusion of electrolytes.** L. J. Kurtz and A. G. Samartzev (J. Phys. Chem. U.S.S.R., 1934, **5**, 1424—1428).—Changes of concn. of the layers near the electrodes during electrolysis were measured with a polarising microscope and Lebedev interferometer. Vals. for the diffusion coeff. of $ZnSO_4$ are given. Ch. Abs. (*e*)

**Viscosity of aqueous solutions of electrolytes as a function of concentration. III. Cæsium iodide and potassium permanganate.** G. Jones and H. J. Fornwalt (J. Amer. Chem. Soc., 1936, **58**, 619—625; cf. this vol., 22).—Determinations have been made at 0° and 25° over a wide range of concn. The variation of *d* with concn. can be expressed by Root's equation. CsI is more effective than any other known salt in lowering the $\eta$ of $H_2O$; the effect is an additive property of the ions. $KMnO_4$ reduces the $\eta$ of $H_2O$. The influence of interionic attraction on $\eta$ is discussed. E. S. H.

**Abnormal vapour pressures in potassium chloride solutions.** A. R. Weir (Coll. Czech. Chem. Comm., 1936, **8**, 149—169).—The v.p. of aq. KCl solutions has been studied by (*a*) determination of the rate of distillation or condensation of $H_2O$ in the capillary limb of an inverted U-tube, the wide limb of which contains the solution at a different temp.; (*b*) passing air through the solution, then over $P_2O_5$, and weighing; (*c*) direct determination of the v.p. of solutions prepared in vac. Solutions containing 58 g. of KCl per 1000 g. of $H_2O$ exhibit variable and abnormally high v.p., indicating the presence of a metastable condition. Data relating to other physical properties at this concn. show similar variations. R. S.

**Positive platinum sols.** N. Bach and N. Balaschowa (Nature, 1936, **137**, 617).—These have been prepared by the regulated oxidation of negative $H_2$–Pt sols. The particles behave like small Pt gas electrodes. Cataphoretic velocities of the sols corresponding with different degrees of oxidation are recorded. L. S. T.

**Colloidal solutions in concentrated electrolytes.** A. Voet (J. Physical Chem., 1936, **40**, 307—315).—Sols of Pd, Pt, Au, and their sulphides, AgCl, AgBr, AgI, C, and S in 96% $H_2SO_4$ or 87% $H_3PO_4$ may remain stable for several weeks. In some cases slow pptn. occurs, but the ppt. can be redispersed by shaking. Stable sols of some of the above have also been prepared in saturated solutions of $CaCl_2$ and KOAc. Dilution with $H_2O$ invariably results in irreversible coagulation. The stability is not due to high viscosity, nor can cataphoresis of the particles be observed. The solutions all show a high electrical conductivity compared with ordinary sols. It is suggested that stability is due to solvation. F. L. U.

**Relation between electro-chemical constitution and colloid structure of pure dyes sols.** W. Pauli and F. Lang (Monatsh., 1936, **67**, 159—186).—By electro-dialysis and electro-decantation, very pure blue acidoid dye sols have been prepared from Congo-red (I), Congo-rubin (II), Congo-corinth G (III), benzopurpurin 4B (IV), and Chicago-blue 6B (V), the variation of their mol. conductivity with temp. and dilution being studied and compared with that of the basic dye sol of night-blue. The energy of association increases with increased internal salt formation and with the increase in polar acid groups arising from ammonolysis of the internal salt. Association hysteresis occurs and equilibrium vals. of the conductivity are obtained only after keeping at any prescribed temp. (II) and (III) have a greater conductivity than (I); this is attributed to the presence of OH in place of $NH_2$. The behaviour of (IV) and (V) is also in accord with their respective constitutions. The structure of dye sols and their relation to soap and protein sols are discussed. J. W. S.

**Production of oxide cathodes of colloidal structure.** E. Patai and Z. Tomaschek (Kolloid-Z., 1936, **75**, 80—88; cf. this vol., 566).—Hydrosols of alkaline-earth carbonates are prepared by leading $CO_2$ into $Ba(OH)_2$ dissolved in aq. glycerol or $(CH_2{\cdot}OH)_2$. The sols are suitable for electrophoretic deposition on metals to give oxide cathodes. E. S. H.

**Highly-polymerised compounds. CXXXIV. Distribution of mol. wts. in highly-polymerised mixtures and determination of mean mol. wt.** G. V. Schulz (Z. physikal. Chem., 1936, B, **32**, 27—45; cf. this vol., 314).—The relations between the frequency and mass distribution functions and the mean mol. wt., *M*, are deduced mathematically. By means of the distribution function the difference between the average mol. wt. of a mixture of polymeride homologues determined viscosimetrically and *M* can be calc. The distribution functions of a polystyrene fraction, a polymerised *iso*butylene (I), and a cellulose nitrate (II) of high mol. wt. have been determined. Calculation of the difference between the viscosimetric mol. wt. and *M* has shown that in the determination of the mol. wt. by the viscosimetric method the presence of moderate amounts of other polymerides does not cause notable error. The difference in the distribution functions of (I) and (II) indicates that the processes by which cellulose is elaborated in the plant and the synthetic polymeride formed are fundamentally different. Staudinger's viscosity law is valid to within a few % for cellulose and substances of similar structure for degrees of polymerisation of 10—1000. R. C.

**Structures of precipitates. II. Effect of $Mg^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Cu^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, and $Cd^{\cdot\cdot}$ ions on peptisability of secondary particles of barium sulphate precipitates. III. Occlusion phenomena with barium sulphate precipitates.** B. TEŽAK (Z. physikal. Chem., 1936, B, 32, 46—51, 52—64; cf. this vol., 427).—II. The peptisability of $BaSO_4$ pptd. from a mixture of aq. $BaCl_2$ and $XSO_4$ of concns. 0·02—0·05*N* decreases as X is varied in the order $Mg^{\cdot\cdot} > Zn^{\cdot\cdot} > Ni^{\cdot\cdot} > Cu^{\cdot\cdot} > Mn^{\cdot\cdot} > Cd^{\cdot\cdot}$. It is related to the sorption of these ions on the $BaSO_4$ and to their hydration.

III. The effect of variation of the conditions of pptn. on the amount of Cl occluded by the ppt. formed from $BaCl_2$ and $Na_2SO_4$ has been studied. It appears that the occlusion is due to adsorption on the primary particles. The ions present as complementary ions in the adsorption layer may considerably influence the composition of the primary adsorption layers of the lattice ions; *e.g.*, in pptn. with $Ba(NO_3)_2$ the $NO_3'$ ions may cause preferential adsorption of $Ba^{\cdot\cdot}$, the ppt. being charged positively, whereas with $BaCl_2$ as precipitant under similar conditions the ppt. is negatively charged owing to preferential adsorption of $SO_4''$ ions. R. C.

**Viscosity and lyotropic numbers** E. M. BRUINS (Rec. trav. chim., 1936, 55, 297—300).—A reply to Merckel (this vol., 426). E. S. H.

**Directed coagulation in aërosols.** D. BEISCHER and A. WINKEL (Z. physikal. Chem., 1936, 176, 1—10).—An aërosol of dimethylaminoazobenzene coagulates at a rate essentially in accordance with Smoluchowski's theory. With an aërosol of aminoazobenzene (I) the coagulation coeff. is exceptionally large, and the relation between $1/n$ and $t$ becomes linear only after coagulation has proceeded for some time. This anomaly is due to the pyro-electric properties of (I). Condensation of the vapour yields crystals of colloidal dimensions in which on cooling a pyro-electric moment appears, and the particles attract and orient each other, giving long strings consisting of up to 50 particles joined end to end. Certain foreign substances inhibit the pyro-electric effect, and coagulation is then normal. A method of determining pyro-electric moments is described which consists in observing the deflexion produced when a homogeneous electric field is applied to a crystal suspended by a quartz fibre. R. C.

**Influence of alkalinity of glass on the viscosity of dilute solutions of cellulose nitrate in ether–alcohol.** J. GRÉVY (Compt. rend., 1936, 202, 480—482; cf. A., 1935, 581).—The viscosity ($\eta$) of 0·3% solutions of cellulose nitrate in $Et_2O$–EtOH (EtOH 60 wt.-%) kept in glass vessels decreases at a rate depending on the nature of the glass and the extent of the surface of contact. It is greatest with ordinary glass cleaned with $H_2O$, and least for Pyrex glass cleaned with $CrO_3$ and $H_2SO_4$. Experiments in which small amounts of $K_2CO_3$ or $Na_2CO_3$ were added indicate that the alkalinity of the glass is responsible. F. L. U.

**Viscosity measurements during the coagulation of titanium dioxide sol by mixtures of electrolytes and non-electrolytes.** (MISS) O. JOSEPH and S. M. MEHTA (J. Univ. Bombay, 1935, 4, Part II, 123—131).—The influence of MeOH, EtOH, and PrOH on the changes with time of the viscosity of $TiO_2$ sol, dialysed to different extents, on addition of KCl, $MgCl_2$, and $AlCl_3$ has been investigated. In each case the viscosity increases on addition of alcohol, in accord with the view that the dielectric const. of the medium is reduced and hence the density of charge on the particle, with consequent increased hydration. The addition also increases the rate of coagulation, indicating that either the rate of aggregation or the rate of hydration of the particles is increased. The periodic nature of the viscosity–time curve decreases with increasing purity of the sol. J. W. S.

**Coagulation of dilute oil emulsions by mercuric chloride: evidence for the discontinuity of the change in the slow region.** S. S. JOSHI and S. P. SARKAR (J. Univ. Bombay, 1935, 4, Part II, 140—145).—The coagulation of oil emulsions has been studied from variations in viscosity ($\eta$), transparency, and refractive index. The discontinuities in the $\eta$-time curve are the more pronounced the lower is the electrolyte concn. The coagulation is always accompanied by a small initial decrease in $\eta$ during the first 20—30 min., resulting in some cases in a nett decrease in $\eta$ during coagulation. The change in transparency is rapid initially, but becomes almost zero in later stages. The refractive index decreases during coagulation, and this tendency is the greater the higher is the electrolyte concn. The results are only partly in accord with the view that the refractivity approximates to that of the continuous medium, modified by the presence of electrolyte. In some cases the change in refractive index is also discontinuous. J. W. S.

**Electrolyte coagulation of weakly solvated sols and electrolyte activity. II. Influence of sol concentration on flocculation value.** WO. OSTWALD (Kolloid-Z., 1936, 75, 39—59; cf. this vol., 157).—A crit. discussion of published data. Increase of sol concn. may (*a*) sensitise the sol to univalent ions and stabilise it to multivalent ions (typical of hydrophobic sols), (*b*) stabilise the sol to all types of electrolytes (metal hydroxide sols, Prussian-blue, etc.), or (*c*) sensitise the sol to all electrolytes ($NH_2Ph$–$H_2O$ emulsions). Flocculation vals. are considered in terms of the activity coeffs. of the dominating ions. E. S. H.

**Viscosity of suspensions and solutions. V. Influence of Brownian movement on the viscosity of ellipsoid suspensions.** E. GUTH. **VI. Viscosity of rod-like suspensions.** F. EIRICH, H. MARGARETHA, and M. BUNZL (Kolloid.-Z., 1936, 75, 15—20, 20—37; cf. this vol., 562).—V. Mathematical.

VI. Investigation of suspensions containing rod-like particles of glass, or natural or artificial silk shows that the measured viscosity depends on the orientation

of the particles, and thus varies with the streaming velocity and with the design of the viscosimeter.
E. S. H.

**Quantitative relations in the lyotropic series.** E. H. Büchner (Kolloid-Z., 1936, **75**, 1—9).—A crit. discussion of published work. E. S. H.

**Influence of the addition of small quantities of electrolytes on a copper ferrocyanide sol in reference to the flocculation produced by the same electrolytes.** A. Boutaric and (Mlle.) P. Berthier (Bull. Soc. chim., 1936, [v], **3**, 696—701).—Addition of small amounts of LiCl, KCl, or $NH_4Cl$ stabilises the sol towards coagulation by larger amounts of the same electrolytes. The effect depends on the time interval which elapses before the more conc. electrolyte solution is added; protection increases at first as the time interval increases, passes through a max., and finally disappears. The effect is not observed with $CaCl_2$, $BaCl_2$, or $AlCl_3$. E. S. H.

**Problems of the theory of diffusion.** T. Katsurai and K. Kawashimo (Kolloid-Z., 1936, **75**, 37—39).—Mathematical. E. S. H.

**Swelling power of caoutchouc in solvent mixtures in relation to their dielectric polarisation.** N. Jermolenko and S. Levina (Kolloid-Z., 1936, **75**, 59—65).—The swelling of caoutchouc in binary mixtures of $H_2O$, $CCl_4$, $C_6H_6$, PhMe, $PhNO_2$, $COMe_2$, EtOH, and $CHCl_3$ has been examined. In mixtures of two polar or non-polar solvents the swelling is parallel to the change in mol. polarisation of the mixture. The effects are irregular in mixtures of polar with non-polar solvents, but in some cases the degree of swelling is in the opposite sense to the change in mol. polarisation. The swelling of caoutchouc in $C_6H_6$–$CHCl_3$ is increased by addition of EtOH. E. S. H.

**Gelatin dichromate. II.** E. Elöd and H. Berczeli (Kolloid-Z., 1936, **75**, 66—73; cf. B., 1936, 465).—Degradation of gelatin by hydrolysis at 100°, or the addition of gelatin degradation products or albumin, increases the rate of dissolution of gelatin–$(NH_4)_2Cr_2O_7$ and decreases the light-sensitivity.
E. S. H.

**Dilatometric study of various ternary glasses.** E. Rencker (Bull. Soc. chim., 1935, [v], **2**, 1389—1407; cf. A., 1935, 36).—Cubical expansion coeffs. and temp. of transformation have been determined for $SiO_2$–$Na_2O$–X glasses, where X=$Al_2O_3$, BeO, MgO, ZnO, CaO. The law of additivity of expansion coeffs. of Winkelmann and Schott (Ann. Physik, 1894, **51**, 735) was found applicable within 3%, in all melts except those containing $>15\%$ $Al_2O_3$, but the coeffs. for the individual oxides given by these authors, and by English and Turner (B., 1928, 262), do not accord either with one another or with the present measurements, and a new set of vals. are calc. Partial replacement of the $SiO_2$ in a $SiO_2$–$Na_2O$ glass by X raises the transformation temp. in the order: ZnO, CaO, MgO, $Al_2O_3$, BeO; glasses containing more than 15% BeO devitrify on cooling, due to their high basicity. R. C. M.

**Inertia and chemical activity of the rare gases. VI. Elimination of helium from the compound platinum–helium and from radium salts at different temperatures.** H. Damianovich (Anal. soc. cient. Argentina, 1934, **118**, 227—241; cf. A., 1934, 1296).—It is suggested that He which can be eliminated from Ra salts by heating is held by certain impurities, in a combination of the type found in the Pt–He compound. Ch. Abs. (*e*)

**Influence of foreign substances on fluorescent power. Colourless inhibitors.** J. Bouchard (J. Chim. phys., 1936, **33**, 325—344).—Increase of mol. association by the addition of electrolytes (I) to a conc. solution of fluorescent substance (II) decreases the fluorescent power. Variation of fluorescent power with the concn. of (II) follows an exponential law the more closely the greater is the concn. of (I). *k* (cf. this vol., 408) increases with concn. of (I), but in very conc. solutions only of (II) in conditions where a modification of the absorption spectrum of dissolved (II) appears. Expressions relating the action of a large no. of colourless org. and inorg. inhibitors (III) on uranine solutions (IV) to the concn. of (III) and (IV) are given. The *h* of (III) diminishes with decreasing dielectric const. and with increasing *n*. In general *h* varies parallel with *k*. The most active (III) are typical antioxidants. Relative vals. of *h* for different (III) vary with (II). M. S. B.

**Dissociation of strong electrolytes in concentrated solutions.** I. R. Rao and C. S. Rao (Nature, 1936, **137**, 580).—Raman spectra indicate that (i) all oxy-acids dissociate progressively with increasing dilution, (ii) the halogen acids are completely dissociated even in conc. solutions, (iii) the acid salts of the alkalis are completely dissociated into alkali ion and the acid radical, the further dissociation of which is progressive, and (iv) all other salts of the alkalis and alkaline earths are completely dissociated even in saturated solutions. An explanation of these results based on the electronic theory of valency is discussed.
L. S. T.

**Effect of ionic charge on acidity of an acid.** G. Schwarzenbach (Z. physikal. Chem., 1936, **176**, 133—153).—Experimental evidence is adduced to show that the difference in acidity between two acids which differ only by an ionic charge, *i.e.*, the nuclear charge of some atom in the mol., is solely a function of the distance between the seat of this charge and the seat of the proton which is released from the acid; there is no evidence of any influence exerted by an electrostatic difference between the acid groups of the two acids. This is also generally true when the ionic charge by which the acids differ is a proton. It thus becomes possible to calculate from the difference in acidity the work done in separating the acid proton from the ionic charge, and in this way an experimental potential curve for the vicinity of an ionic charge in a polar medium may be derived. This curve differs from $e^2/rD$. The above considerations have been utilised to calculate the acidities of certain acids which cannot be examined experimentally. R. C.

**Influence of a substituent on the acidity of an organic acid. II.** G. Schwarzenbach and A. Epprecht (Helv. Chim. Acta, 1936, **19**, 493—504).—Normal acidity potentials have been determined at

20° for $EtCO_2H$, $CHEt_2\cdot CO_2H$, $CHPr_2\cdot CO_2H$ and for the $Et_1$ esters of malonic, diethyl- and dipropylmalonic acids in 18·1—95·0 vol.-% EtOH. It is concluded that electrostatic effects are mainly absent and that the influence of the substituents considered is electronic (cf. A., 1934, 1310). The mechanism of the electronic effect is discussed. M. S. B.

**First dissociation constant of carbonic acid at various temperatures.** Y. Kauko and J. Carlberg (Z. physikal. Chem., 1936, **176**, 11—19).—The first dissociation const. at 0—25° has been determined by $p_H$ measurements on aq. $NaHCO_3$ through which $CO_2$ is passing. The results agree with those of Kendall (A., 1916, ii, 512), but not with those of MacInnes *et al.* (A., 1935, 1321). R. C.

**Anomalies in the dissociation constant of some halogenated organic acids. III.** M. Betti and E. Lucchi (Atti R. Accad. Lincei, 1935, [vi], **22**, 367—370; cf. this vol., 564).—For the two acids *trans*-$C_6H_4X\cdot CH\colon CH\cdot CO_2H$ (X=Cl and Br) $K$ at 25°=$0{\cdot}39\times10^{-4}$, which is nearly the same as the val. for cinnamic acid ($K=0{\cdot}365\times10^{-4}$). O. J. W.

**Quantitative investigations of amino-acids and peptides. II. Apparent dissociation constants in aqueous formaldehyde solution.** M. S. Dunn and A. Loshakoff (J. Biol. Chem., 1936, **113**, 691—694; cf. this vol., 620).—Vals. of $pK'_a$ in aq. $CH_2O$ of a no. of $NH_2$-acids have been determined. H. D.

**Differential dissolution of sodium bromide in its aqueous solutions and the activity coefficients of sodium bromide in concentrated aqueous solutions.** F. Murata (J. Chem. Soc. Japan, 1935, **56**, 588—595).—The e.m.f. of the cell Na (amalgam, 0·2203%)|NaBr,aq. ($m$), HgBr|Hg has been determined for various vals. of $m$ and of temp. The free-energy change in the differential dissolution of NaBr in aq. solution and the activity coeff. are calc. The heat of dissolution of $NaBr,2H_2O$ at 25° is —2933 g.-cal. Ch. Abs. (*e*)

**Thermodynamic properties of cadmium sulphate in aqueous alcohol.** V. K. LaMer and E. L. Carpenter (J. Physical Chem., 1936, **40**, 287—302; cf. A., 1934, 31).—The influence of increasing EtOH content on the partial free energy, heat content, and heat capacity of $CdSO_4$ in aq.-EtOH solution has been determined. The val. of the mean ionic radius of the ions, calc. from the Born equation, agrees fairly with that of the distance of closest approach calc. by the extended theory of Debye and Hückel. F. L. U.

**Selenites of sodium, potassium, and ammonium in aqueous solution.** J. Janickis and H. Gutmanaite (Z. anorg. Chem., 1936, **227**, 1—16; cf. A., 1932, 584).—Solubilities of Na, K, and $NH_4$ selenites in $H_2O$, and f.p. of the solutions, have been determined down to their respective cryohydric points. Conductivities have been measured between 0·0002$M$ and 2$M$. The normal salts behave as ternary, and $NaHSeO_3$ and $KHSeO_3$, except at great dilution, as binary, electrolytes. The $NH_4$ salt behaves according to: $(NH_4)_2Se_2O_5+H_2O \rightleftharpoons 2NH_4HSeO_3$. The behaviour of the tetraselenites is expressed by: $MH_3(SeO_3)_2 \rightleftharpoons M^{\cdot}+[H_3(SeO_3)_2]' \rightleftharpoons HSeO_3'+H_2SeO_3$. F. L. U.

**Hydrolysis of inorganic salts and chemistry of high-molecular hydrolysis products, including iso- and heteropoly-compounds. III** G. Jander and K. F. Jahr (Kolloid-Beih., 1936, **43**, 295—362; cf. A., 1934, 489).—Mainly a crit. summary of published work, with additional experimental data relative to the diffusion, conductivity, and light absorption of aq. salts of Mg, Zn, $VO_2^{II}$, Be, Al, $ZrO^{II}$, $Fe^{III}$, and $Cr^{III}$. E. S. H.

**Polarimetric study of nickel malate.** J. L. Delsal (Compt. rend., 1936, **202**, 1280—1282).—When NaOH is added to solutions containing $Ni(NO_3)_2$ and excess of malic acid, the rotatory power passes through min. and max. vals., corresponding with the formation of Ni malate and Na nickelomalate, respectively. The formation of a sol. complex nickelomalic acid is indicated. L. J. J.

**Application of thermodynamics to chemical equilibria in homogeneous systems.** M. W. Mund (Ann. Soc. Sci. Bruxelles, 1936, **56**, B, 15—34).—Theoretical. M. S. B.

**Diagrams representing physico-chemical analyses of irrational systems.** M. Usanovitsch (J. Gen. Chem. Russ., 1935, **5**, 1757—1761).—Polemical, in reply to Ust-Katschkintzev (this vol., 22). R. T.

**Heterogeneous gaseous equilibria $NaCl+HBr \rightleftharpoons NaBr+HCl$ and $KCl+HBr \rightleftharpoons KBr+HCl$.** K. Jellinek, W. Wlodarski, and T. Arczynski (Z. anorg. Chem., 1936, **227**, 43—51; cf. this vol., 674).—Equilibria in the system NaCl+HBr have been determined at 850—950°, and in KCl+HBr at 765—850°. In both the condensed phase is homogeneous liquid [(Na, K)Cl+(Na,K)Br] which behaves as an ideal mixture. Heats of reaction are calc. F. L. U.

**Equilibria $Cl_2+2KBr \rightleftharpoons 2KCl+Br_2$ and $Br_2+Cl_2 \rightleftharpoons 2BrCl$.** K. Jellinek and H. Schütza (Z. anorg. Chem., 1936, **227**, 52—61; cf. A., 1933, 783).—Determination of the equilibrium const. in the above reactions at 800° gives $N^2_{KCl}p_{Br_2}/N^2_{KBr}p_{Cl_2}=303$, and $p_{Cl_2}p_{Br_2}/p^2_{BrCl}=0{\cdot}12$ ($N$=mol. fraction, $p$=partial pressure). The dissociation const. for BrCl is nearly independent of temp. F. L. U.

**Equilibrium diagram of the system barium fluoride–magnesium fluoride.** U. Nisioka and M. Okamoto (Kinz.-no-Kenk., 1935, **12**, 220—225).—Data are recorded. The *compound* $BaF_2,2MgF_2$ is formed. It forms a eutectic with $BaF_2$ at 912° (17% $MgF_2$). A glassy mass could not be obtained by quenching the melt. Ch. Abs. (*e*)

**Dissociation pressure of cupric sulphate pentahydrate.** K. Sano (Sci. Rep. Tôhoku, 1936, **24**, 719—723).—Measurements have been made by a statical method using Jackson's glass-spring manometer at 48—82° and the results are in fair agreement with earlier ones obtained in the tensimeter. The relation $\log P_{H_2O}=-2{,}894{\cdot}47/T+10{\cdot}611$ holds. Thermodynamical data for the reaction $CuSO_4,5H_2O=CuSO_4,3H_2O+2H_2O$ are $\Delta F^\circ_{298}$ 5146 g.-cal., $\Delta H^\circ_{298}$ 26,578 g.-cal., and $\Delta S^\circ_{298}$ 71·01 e.s.u. M. S. B.

**Dissociation of smithsonite.** R. Mehmet and G. Valensi (Bull. Soc. chim., 1935, [v], **2**, 1295—

1300).—Decomp. pressures obtained by the static method at 250° and 290°, are > those given by Centnerszwer's dynamic method (A., 1924, ii, 655), but much < the equilibrium vals. calc. from published heats of dissociation, due to the low rate of decomp. below 300°. The formation of a solid solution of ZnO in $ZnCO_3$ is improbable. R. C. M.

**Mutual relation between silicates and sulphides.** A. S. Ginsberg (Trav. Inst. pét. Acad. Sci. U.R.S.S., 1933, 4, 21—45).—The systems $Fe_2SiO_4$–FeS, $MnSiO_3$–FeS, and $Mn_2SiO_4$–FeS have been studied. The components are characterised by limited miscibility in the liquid state. Ch. Abs. (*c*)

**Equilibria of metal fluorides with water vapour.** L. Domange (Compt. rend., 1936, 202, 1276—1277; cf. A., 1935, 448, 1088).—Data are recorded for equilibrium HF–$H_2O$ concns. with a no. of fluorides at high temp. Heats of reaction at const. pressure are calc. from the data. L. J. J.

**Equilibrium diagrams of the systems (A) $CaO,Al_2O_3,2SiO_2$–$CaO,TiO_2$, and (B) $CaO,MgO,2SiO_2$–$CaO,TiO_2$.** U. Nisioka (Sci. Rep. Tôhoku, 1936, 24, 707—713, 714—718).—(A) The quenched mixtures were examined microscopically under reflected light. There is an eutectic at 1350° and 35% $CaO,TiO_2$ by wt.

(B) There is a simple eutectic at 1270° and 32% by wt. of $CaO,TiO_2$. M. S. B.

**Equilibria in the system cobalt sulphate–sulphuric acid–water.** L. L. Kljatschko-Gurvitsch and H. Ogandshanova (J. Gen. Chem. Russ., 1935, 5, 1781—1785).—Solubility data are recorded for $CoSO_4$ in $H_2O$ and aq. $H_2SO_4$ at 0° and 20°. Crystallisation of $CoSO_4,7H_2O$ is at a max. in presence of 35% $H_2SO_4$ at 0°, and of 26·8% at 20°. R. T.

**Thermodynamic study of systems of the type $PbCl_2$–RCl–$H_2O$ at 25°.** A. R. Weir (Coll. Czech. Chem. Comm., 1936, 8, 93—113).—$H_2O$ activities have been derived from measurements of the v.p. of solutions of widely varying concns. Abnormal changes of v.p. are found in the vicinity of the system with $PbCl_2$ and $KCl,2PbCl_2$ as solid phases. J. G. A. G.

**Systems antimony (or bismuth) iodide–alkali iodide–water.** F. François and M. L. Delwaulle (Bull. Soc. chim., 1936, [v], 3, 687—696).—Equilibrium data at 12—16° have been obtained. The systems contain many double salts, which are isomorphous when Sb is replaced by Bi. Interchange of alkali metal (Na, K, Li, $NH_4$) may produce double salts of different type. E. S. H.

**Thermochemistry of titanium oxides. I. The equilibrium, $2TiO_2+H_2 \rightleftharpoons Ti_2O_3+H_2O$.** N. Nasu (J. Chem. Soc. Japan, 1935, 56, 542—551).—The heterogeneous equilibrium was studied at 1022—1282° abs. Ch. Abs. (*e*)

**Heats of combustion and sublimation.** H. C. Blanck and K. L. Wolf (Z. physikal. Chem., 1936, B, 32, 139—144).—These quantities have been determined for succinic acid and several derivatives. The results show that of the esters of the isomeric tartaric acids the meso-compounds have the greatest internal energy contents, which is ascribed to difference in the extent of intramol. association of the OH groups. R. C.

**Dissociation energies of carbon monoxide and CN, and heat of sublimation of carbon.** G. Herzberg (Nature, 1936, **137**, 620).—Brons' val. of 193·9 kg.-cal. for $D_{CO}$ (this vol., 8) is not necessarily correct; a val. of 209·7 kg.-cal. is also compatible with available pre-dissociation data, and gives a val. for the heat of sublimation of C, viz., 125·1 kg.-cal., more in keeping with the val. of 143 kg.-cal. obtained from thermal data. L. S. T.

**Electric conductivity of the system acetic anhydride–water.** N. A. Trifonov and V. F. Ust-Katschkintzev (J. Phys. Chem. U.S.S.R., 1934, 5, 1215—1221).—Measurements at 0°, 50°, and 72·5° show max. at 3·5—4·5 and 90, and a min. at 50, mol.-% of $Ac_2O$. The temp. coeff. of conductivity has a max. at 50 mol.-%. Formation of AcOH is indicated. Ch. Abs. (*e*)

**Nature of the glass electrode potential. I.** H. Yoshimura (J. Biochem. Japan, 1936, 23, 91—100).—The deviation of the slope of the calibration line of $E$ against $p_H$, $(E_1-E_2)/(p_{H_1}-p_{H_2})$, from the theoretical is shown (by coating with paraffin wax) to be due, not to the "deviation film" of liquid on the non-immersed part of the electrode, but to the nature of the glass membrane, every part of which has its own val. of $E$, the observed $E$ being the average of all parts in proportion to their respective $\kappa$. F. O. H.

**Electrolytic polarisation capacity and the atomic mechanism of hydrogen electrodes.** T. Noguchi (J. Electrochem. Assoc. Japan, 1935, 3, 141—149).—Data for the polarisation capacity of Pt electrodes dipped in $H_2SO_4$ are given. A discharged atom should be deposited on a Pt atom in the surface at. grating of the electrode. The H absorbed by Pt should, at the higher c.d., increase the active surface of the electrode. Ch. Abs. (*e*)

**Influence of light on electrode potential and corrosion phenomena of certain non-ferrous metals.** C. O. Bannister and R. Rigby (J. Inst. Metals, 1936, **56**, Advance copy, 91—108).—Apparatus for continuously recording changes of e.m.f. when an electrode is illuminated under the influence of a regulated supply of $O_2$ is described. The effect of light is considerable in the case of Al, Pb, and Zn in the presence of $O_2$, the aërated and illuminated electrode becoming more cathodic. The max. light effect is shown by violet and near ultra-violet light; the observed effects are attributed to the catalytically accelerated formation of protective oxide films. A. R. P.

**Diffusion potentials and ionic activities.** J. J. Hermans (Z. physikal. Chem., 1936, **176**, 55—64).—Correction of Nernst's diffusion potential formula to allow for interionic forces gives as the limiting law for infinite dilution $\epsilon=[(l_1-l_2)(l_1+l_2)](RT/F)(\log c+A\sqrt{c})$, where $A$ is a const. which can be calc. from known magnitudes. This expression is compatible with the assumption that at high dilutions the ionic activity coeffs. of HCl are equal. The deductions of Szabó (A., 1935, 1323) are criticised. R. C.

**Ionic activities of sodium and potassium chlorides.** Z. Szabó (Z. physikal. Chem., 1936, **176**, 125—130).—The equation for diffusion potential deduced theoretically by Hermans, taking account of interionic forces (preceding abstract), gives for the experimentally accessible concn. range of 0·0005—$0{\cdot}02M$ the same results for HCl as the author's empirical equation (A., 1935, 1323, 1325). For KCl|KCl up to $M$ the diffusion potential may be represented by the empirical equation $\epsilon=1{\cdot}04 \log (m_1/m_2)$ indicating that the ionic activities are equal even in conc. solutions. For NaCl|NaCl the equation is $\epsilon=12{\cdot}31 \log (m_1/m_2)$ up to $0{\cdot}5M$, also indicating equality of the ionic activities. R. C.

**Diffusion potentials and ionic activities.** J. J. Hermans (Z. physikal. Chem., 1936, **176**, 131—132).—Polemical against Szabó (preceding abstract). A method of determining diffusion potentials at high concns. without using ionic activities is suggested. R. C.

**Polarographic studies with the dropping mercury electrode. IV. Measurement of the polarisation capacity.** D. Ilkovič (Coll. Czech. Chem. Comm., 1936, **8**, 170—177; cf. this vol., 430).—The polarisation capacity $k$ of the dropping Hg electrode has been determined polarographically using the relation $Q=qk\pi$, where $Q$ is the quantity of electricity, $q$ the surface of the drop, and $\pi$ the potential. With cathodic polarisation in $0{\cdot}1N$-KCl, $k=22{\cdot}3\times10^{-6}$ and with anodic polarisation $k=42{\cdot}2\times10^{-6}$ farad per sq. cm. In very pure solutions the Hg sometimes acquires the potential of a reversible H electrode. R. S.

**Polarographic studies with the dropping mercury cathode. LVIII. Electro-reduction of dicyanogen and oxamic acid.** J. Březina and J. Heyrovský (Coll. Czech. Chem. Comm., 1936, **8**, 114—124).—In aq. solutions of NaOAc, $C_2N_2$ causes an increase of current when the potential of the dropping Hg cathode is $-1{\cdot}15$ volt with respect to the $N$-$Hg_2Cl_2$ electrode; this is attributed to direct electro-reduction of $C_2N_2$. The second increase of current at $-1{\cdot}55$ volt is probably due to electro-reduction of oxamic acid or its salt. As the age of the solution increases, the first polarographic "wave" diminishes and the second increases. $C_2N_2$ has no effect on current-voltage curves of alkaline solutions, and in neutral or slightly acid solutions the second "wave" develops slowly but does not appear in more acid solutions. The results are interpreted in terms of the hydrolysis of $C_2N_2$. $10^{-5}$—$10^{-6}$ g.-mol. per litre of $C_2N_2$ and oxamic acid can be detected polarographically. J. G. A. G.

**Theory of passivity. XXIX. Theory of the barrier layer in aluminium.** W. J. Müller [with E. Löw] (Z. Elektrochem., 1936, **42**, 166—175; cf. A., 1935, 1326).—The formation of an oxide layer on specially pure (99·998%) Al immersed in saturated aq. $NaHCO_3$ is much more rapid than when ordinary "pure" Al is used, and smaller residual currents are observed. With an applied p.d. $<$ 2 volts conduction is not unidirectional, whilst above this the cathodic current is several hundred times $>$ the anodic. The effect is not due to formation of gaseous $O_2$, but is fully explained by the electro-osmotic theory. F. L. U.

**Electrochemical investigation of [mixed solutions of] aluminium and potassium bromides in solvent mixtures.** V. A. Plotnikov, O. K. Kudra, and J. F. Mejenny (Z. physikal. Chem., 1936, **176**, 154—159).—The decomp. voltages of solutions in EtBr and PhMe increase considerably on addition of small amounts of $PhNO_2$; further additions have a smaller effect. For an equimol. ratio of $AlBr_3$ to $PhNO_2$ the conductivity in dil. solutions is a max. and in conc. solutions a min. It is inferred that a complex containing $AlBr_3$, KBr, and $PhNO_2$ is present in solution. On electrolysis a coherent deposit of K separates on the cathode; with certain solvents the current yield may rise to 40%. R. C.

**Dissociation constants of reductone and of its product of oxidation by iodine.** G. Carpéni (Compt. rend., 1936, **202**, 1065—1067).—The dissociation const. of reductone [OH·CH:C(OH)·CHO] at 20±0·5° is $1{\cdot}17\times10^{-5}$, as calc. from titrimetric data. The NaOH titrimetric curves for the solution obtained by oxidising reductone with aq. I give a dissociation const. $2\times10^{-4}$ ($K_1$), in agreement with oxidation-reduction potentials (cf. this vol., 292). With $p_H > 4{\cdot}6$ the p.d. after each addition of NaOH falls exponentially; the decrease is at first small, but becomes large at $p_H$ 6—9·5. After 24—48 hr. the equilibrium mixture gives a second dissociation const. $2{\cdot}5\times10^{-6}$ ($K_2$). A return titration by HCl gives a new curve which is not modified by a new titration with NaOH; this curve shows an exaltation of acidity, $K_1$ and $K_2$ becoming $5\times10^{-4}$ and $6{\cdot}8\times10^{-5}$, respectively. A parallel is drawn with the behaviour of oxyascorbic acid. R. S. B.

**Nature of complexes of phenols with amines.** L. P. Kulev (J. Gen. Chem. Russ., 1935, **5**, 1566—1575).—The e.m.f. developed when Na and Pt electrodes are immersed in PhOH in $C_6H_6$ in presence of $C_5H_5N$ is at a max. for 25—30% of PhOH. At this concn. in absence of $C_6H_6$ the e.m.f. is at a min., but rises on progressive addition of $C_6H_6$ to the $C_5H_5N$ solution. $H_2O$, $PhNO_2$, and *m*-nitrotoluene have a similar effect, $Pr^{a}OH$, $Bu^{a}OH$, and $Bu^{\gamma}OH$ have the opposite effect, and $Pr^{\beta}OH$ and *o*-nitrotoluene are without action when added to 25% PhOH in $C_5H_5N$, but at other concns. of PhOH the effects of adding these compounds may be entirely different. Of a no. of phenols examined, PhOH is the most active; the activity of the cresols diminishes in the order *m*- $>$ *p*- $>$ *o*-. The above effects are ascribed to formation of mol. complexes, the possible structure of which is discussed. The complexes are more readily formed with $C_5H_5N$ than with $NH_2Ph$ or $NPhMe_2$. The high e.m.f. obtained in presence of $NEt_3$ is considered to be a consequence of formation of the salt $NHEt_3$·OPh. R. T.

**Chemical reaction and atomic theory.** J. M. Bijvoet (Chem. Weekblad, 1936, **33**, 222—231, 270—277).—Theoretical. The factors determining the occurrence and velocity of reactions and the magnitude of equilibrium consts. are discussed in the light of modern developments of wave mechanics. D. R. D.

**Calculation of intermediate reactions in homogeneous systems.** A. Skrabal (Z. Elektrochem., 1936, **42**, 228—246).—Mathematical. Complete reaction schemes are developed on the basis of the kinetic theory for various types of intermediate reaction (cf. A., 1935, 39, 707, 1328). C. R. H.

**Homogeneous unimolecular decomposition reactions of gases. II.** F. Patat (Z. Elektrochem., 1936, **42**, 265—276).—A further review (cf. this vol., 293).

**Recent developments in reaction kinetics, especially gas explosions.** J. A. Hveding (Tids. Kjemi, 1936, **16**, 50—55).—A review. M. H. M. A.

**Equilibrium constants and velocity constants.** M. G. Evans and M. Polanyi (Nature, 1936, **137**, 530—531).—A generalised expression, from which the known relationship between $k$ and $K$ of certain related chemical reactions can be deduced as specialised cases, is derived from thermodynamic considerations. L. S. T.

**Viscosity, plasticity, and diffusion as examples of absolute reaction rates.** H. Eyring (J. Chem. Physics, 1936, **4**, 283—291).—Theoretical. L. J. J.

**Absolute rate of reactions in condensed phases.** E. A. Moelwyn-Hughes (J. Chem. Physics, 1936, **4**, 292). H. Eyring and W. F. K. Wynne-Jones (*ibid.*, 293; cf. A., 1935, 1205).—Criticism and a reply. L. J. J.

**Influence of pressure, concentration, and temperature on the speed of the slow oxidation and the ease of spontaneous inflammation of mixtures of oxygen and *n*-pentane below 300°.** M. Prettre (Compt. rend., 1936, **202**, 954—956).—Increase in the initial pressure in a 36% $C_5H_{12}$–$O_2$ mixture shortens the lag before ignition. The min. lag was observed in an equimol. mixture. H. J. E.

**Slow combustion of benzene and other hydrocarbons.** J. Amiel (Compt. rend., 1936, **202**, 946—948).—The fraction of $C_6H_6$ oxidised at a time $t$ and temp. $T$ is given empirically by $\gamma=10^{(A/T)+B}t-10^{CT+D}$. Similar expressions are valid for the oxidation of $C_2H_2$ or $C_3H_8$. H. J. E.

**Decomposition of azomethane. I. Apparatus.** D. V. Sickman and O. K. Rice. **II. Pure azomethane and azomethane in presence of helium.** O. K. Rice and D. V. Sickman (J. Chem. Physics, 1936, **4**, 239—241, 242—251).—I. A manometer adapted to the measurement of small changes in a large total pressure is described.

II. Kinetic data at 290° and 310° are recorded for $p_{Me_2N_2}$ 0·35—25 mm. and $p_{He}/p_{Me_2N_2}$ 5 and 10. The pressure dependence of $k$ is in better agreement with the theory of Rice, Ramsperger, and Kassel than are Ramsperger's results (A., 1927, 737). He has an activating efficiency 0·120 of that of $Me_2N_2$. The evidence is against a chain mechanism. L. J. J.

**Mechanism of thermal reaction between gaseous iodine monochloride and hydrogen.** A. Sherman and N. Li (J. Amer. Chem. Soc., 1936, **58**, 690—691).—Theoretical. E. S. H.

**Flame speeds in moist carbon monoxide-oxygen mixtures.** V. Voronkov and A. Sokolik (Nature, 1936, **137**, 533—534).—Curves obtained for the speeds of propagation of flame in various $CO+O_2$ mixtures at different pressures are reproduced. Their form is not connected with hygroscopic conditions (cf. this vol., 163), but with a change in the temp. of spontaneous combustion for const. time lag. L. S. T.

**Kinetics of the reaction between hydrogen and sulphur. III. (i) Reaction at 350—412° and 50—150 mm. (ii) Behaviour of sulphur on a hot glass surface.** R. P. Cook and P. L. Robinson (J.C.S., 1936, 454—456).—(i) The kinetics of the reaction are the same as at the lower temp. previously investigated (A., 1935, 307), and the rise of temp. does not increase the heterogeneous reaction (cf. *ibid.*, 586).

(ii) At the reaction temp. employed (*loc. cit.*), liquid S does not "wet" glass in vac. or in an atm. of $H_2$, and does not form a visible film on the internal surface of the reaction vessel (cf. J.C.S., 1923, **123**, 696). J. G. A. G.

**Mechanism of decomposition of ethylene iodide.** R. A. Ogg, jun. (J. Amer. Chem. Soc., 1936, **58**, 607—609).—Theoretical. The kinetic results are explained by a chain mechanism. A similar conclusion is reached for the decomp. of di-iodopropyl alcohol and the photo-bromination of cinnamic acid. E. S. H.

**Kinetics of formation and decomposition of di*cyclo*pentadiene.** B. S. Khambata and A. Wassermann (Nature, 1936, **137**, 496—497).—The reaction *cyclo*pentadiene+*cyclo*pentadiene $\rightleftharpoons$ di*cyclo*pentadiene is bimol. in the direct and unimol. in the reverse directions. No chain mechanism appears to be involved. Measurements of the direct reaction in $C_6H_6$ between 15° and 55° and of the decomp. in paraffin between 135° and 175° show the Arrhenius equation to be valid. L. S. T.

**Relationships between reaction velocities and ionisation constants.** J. F. J. Dippy and H. B. Watson (J.C.S., 1936, 436—440; cf. A., 1935, 1465; this vol., 296).—It follows from accurate vals. of the dissociation consts., $K$, of the acids of the reference series that the supposed linear relationships (*loc. cit.*) are approx. only. Electromeric effects cause divergences, and the connexion does not follow from known relationships of velocity coeffs. and $K$ with dipole moment. The effects of variations in the non-exponential term of the Arrhenius equation are considered. J. G. A. G.

**Kinetic salt effect in fourth-order reaction $BrO_3'+Br'+2H^+\rightarrow$.** M. Sclar and L. C. Riesch (J. Amer. Chem. Soc., 1936, **58**, 667—670).—The rates of reaction in presence of allyl alcohol have been determined at different temp. and ionic strengths and compared with published data. The energy of activation has been calc. The results show that the fourth-order rate-determining reaction is reversible, so that the max. rate of reaction can be obtained only when a primary reaction product is removed with sufficient rapidity to prevent a reversal of the reaction. Allyl alcohol and $H_2O_2$ are equally efficient in removing a primary reaction product. E. S. H.

**Collision frequency in solution: kinetics of diene synthesis in solution and in the gaseous state.** A. Wassermann (Nature, 1936, **137**, 497).—Comparison of the kinetics of various bimol. diene syntheses shows that with slow reactions in solution the collision frequency of mols. is $\nless$ in the gas phase. L. S. T.

**Kinetics of a thermal polycondensation.** H. Dostal and R. Raff (Z. physikal. Chem., 1936, **B**, **32**, 117—129).—The rate of condensation of *p*-cresol with $CH_2O$ in aq. solution at 100—130° has been determined. The energy of activation is about 20 kg.-cal. per mol. Equations for the kinetics of such reactions are deduced theoretically. R. C.

**Reactions between oxalic acid, iodine, and the iodate and iodide ions. III. Kinetics of oxalic acid–iodine reaction.** E. Abel, K. Hilferding, and O. Smetana (Z. physikal. Chem., 1936, **B**, **32**, 85—107; cf. A., 1935, 587).—Determination of the rate, *v*, of $5H_2C_2O_4+2HIO_3=I_2+10CO_2+6H_2O$ at 25—60° has given results agreeing with the mechanism previously suggested (A., 1931, 690). Depending on the concns., *v* varies between two limits, given by $v\propto\sqrt{([IO_3'][I_2][H^{\cdot}]\Sigma)}$ and $v\propto\sqrt[3]{([IO_3'][I_2]^2\Sigma^2)}$ (where $\Sigma=[H_2C_2O_4]+[HC_2O_4'])$, which is in accordance with the above mechanism if it is assumed that for the intermediate products I′ and HIO the stationary and equilibrium concns. are practically equal. The inhibiting action of HCN is due solely to its reaction with the inductor, $I_2$. The velocities of $IO_3'+2H^{\cdot}+I'=HIO_2+HIO$ and $IO_3'+2H^{\cdot}+2I'=2HIO+IO'$ at 50° have been determined. R. C.

**Kinetics of a bimolecular association in benzene solution and in the gaseous state.** A. Wassermann (Nature, 1936, **137**, 707—708).—The reaction between acraldehyde and *cyclo*pentadiene in $C_6H_6$, as in the gaseous state (this vol., 297), is a homogeneous bimol. association. The collision frequency in the gaseous phase is of the same order as the "apparent" collision frequency in solution. L. S. T.

**Progressive elimination of bromine in the aqueous hydrolysis of sodium bromoacetate.** H. Brooke and H. M. Dawson (J.C.S., 1936, 497—504; cf. A., 1933, 1125).—From measurements of the initial velocity of formation of Br′ in mixtures of $CH_2Br\cdot CO_2Na$ (I) and $OH\cdot CH_2\cdot CO_2H$ (II), it is inferred that the hydrolysis $(I)+H_2O\rightarrow(II)+NaBr$ is due to six independent bimol. processes in which $CH_2Br\cdot CO_2'$ (III) or $CH_2Br\cdot CO_2H$ reacts with $H_2O$ or (III) or glycollate ion. Intermediate complexes also affect the rate of the hydrolysis, but the data from the above experiments, which, apart from the absence of complexes, correspond with successive stages of the reaction, are quantitatively explained in terms of the six simple reactions. The complexity of the hydrolytic process is emphasised and the approx. conformity to a unimol. formula is accidental. J. G. A. G.

**Sucrose inversion in $D_2O$–$H_2O$.** W. H. Hamill and V. K. LaMer (J. Chem. Physics, 1936, **4**, 294).—*k* in $D_2O$–$H_2O$ mixtures is a linear function of $F_{D^+}=[D^+]/([D^+]+[H^+])$. L. J. J.

**Rate of dissolution of copper in dilute aqueous reagents.** C. V. King and L. Weidenhammer (J. Amer. Chem. Soc., 1936, **58**, 602—607).—Determinations of temp. coeff., influence of rate of rotation of Cu, and variation with viscosity (by adding sucrose) show that the rate of dissolution in $Fe^{III}$ solutions is controlled mainly by diffusion, but that in AcOH solutions mainly by chemical reaction. E. S. H.

**Causes of anomaly in the kinetics of the oxidation of metallic powders.** G. Valensi (Compt. rend., 1936, **202**, 414—416; cf. this vol., 434).—Irregularities in the surfaces of the particles, porosity of the particles, and unevenness of grain size all lead to anomalies in the velocity of oxidation of metallic powders, points of low radius of curvature being most easily attacked, whilst depressions and porous regions become filled with the more voluminous oxide and protected against further attack. J. W. S.

**Atmospheric rusting of iron.**—See B., 1936, 411.

**Catalysis by fusions.** E. W. R. Steacie and E. M. Elkin (J. Amer. Chem. Soc., 1936, **58**, 691—692).—A reply to criticism (cf. this vol., 167). E. S. H.

**Action of esterase in presence of organic solvents.**—See this vol., 637.

**Catalysts for the autoxidation of saturated cyclic hydrocarbons.** R. Dupont (Bull. Soc. chim. Belg., 1936, **45**, 113—122).—The catalytic action of the acetylacetonates of $Fe^{III}$, $Cu^{II}$, $Ce^{III}$, $Mn^{III}$, $Co^{II}$, and $Co^{III}$ on the absorption of $O_2$ by 1 : 4-dimethyl*cyclo*hexane (I) and phenyl*cyclo*pentane (II) has been examined. Two types of reaction curves have been observed, one autocatalytic, always found for (II) and also for (I) when the catalyst concn. is $<1\%$, and the other catalytic and characteristic of (I) for a catalyst concn. $>1\%$. M. S. B.

**Delayed oxidation of cysteine and ascorbic acid.** E. Baur and H. Preis (Z. physikal. Chem., 1936, **B**, **32**, 65—83).—The oxidation by gaseous $O_2$ of cysteine (I) in aq. solution of $p_H$ 7·6 with Cu as catalyst is retarded by low concns. of $Fe^{\cdot\cdot\cdot}$ and $Mn^{\cdot\cdot}$ and accelerated by higher concns., whilst salts of some other metals cause retardation only. In most cases the retardation is related to the inhibitor concn., *c*, by the Baur–Ouellet law, whilst in the others it $\propto c$. Some cations have only an accelerating effect. Anions, org. substances, and some cations have no effect. In the oxidation of ascorbic acid in aq. solution at $p_H$ 5·3 with Cu as catalyst, (I), cystine, and phenylalanine at high dilution cause retardation, whilst other oxidation–reduction systems have no effect. Heavy-metal salts have an indefinite or no effect, and CN′ and I′ bind the catalyst. There is no connexion between the oxidation–reduction potential of the foreign substance and its inhibiting action. The results generally support Baur's mol. electrolysis theory. R. C.

**Preparation of platinum oxide for catalytic hydrogenations.** W. F. Bruce (J. Amer. Chem. Soc., 1936, **58**, 687—688).—The catalyst is prepared

by heating gradually a mixture of $(NH_4)_2PtCl_6$ and $NaNO_3$, and keeping at 500° for 25—30 min.
E. S. H.

**Reactions in thin films.** A. I. Zolin (J. Phys. Chem. U.S.S.R., 1934, 5, 1299—1309).—The hydrogenation of $C_2H_4$ with a colloidal Pd catalyst in presence of saponin occurs in the liquid phase in the walls of the colloidal foam bubbles. The presence of foam, due to the saponin, increases the rate 10 times at room temp. $H_2$ tends to collect in the upper layers of the foam, due to more rapid diffusion.
Ch. Abs. (*e*)

**Effect of promoters on molybdenum catalysts in hydrogenation.** F. E. T. Kingman and E. K. Rideal (Nature, 1936, **137**, 529).—P, Ni, Cr, and Si markedly enhance, whilst Sn and Th depress, the catalytic activity of Mo oxide for the hydrogenation of PhOH at 1 atm.
L. S. T.

**Oxidation of alkali halides by molecular oxygen in presence of mercury and active charcoal.** V. A. Piankov (J. Gen. Chem. Russ., 1935, 5, 1543—1550).—The process $4MX+O_2+2H_2O+2Hg \rightarrow 2HgX_2+4MOH$ takes place when air is bubbled through a solution of alkali halide in presence of Hg; the velocity of the reaction rises in the series $Cl<Br<I$. The reaction is catalysed by active C, in presence of which max. velocity is attained at 50°.
R. T.

**Promoter concentration and catalysis.** R. H. Griffith (Nature, 1936, **137**, 538).—For the decomp. of $C_6H_{14}$ at 500° by Mo oxide catalysts the ratio of the no. of atoms of Na, Cr, Ce, Al, Ba, B, and Th (as oxides) to the no. of atoms of Mo necessary for max. promoter action is the same as that observed with Si (B., 1935, 292). With easily reducible oxides, *e.g.*, those of Pb, Fe, or Cu, the promoter concn. required is one half. For the conversion of PhOH into $C_6H_6$ by hydrogenation at 450°/1 atm. with Mo oxide as catalyst the optimum concn. is > in the above reaction, but is practically the same for $SiO_2$ and $Al_2O_3$.
L. S. T.

**[Catalytic] synthesis of higher alcohols under pressure.**—See B., 1936, 404.

**Carbon oxysulphide.** J. Milbauer (Z. Elektrochem., 1936, **42**, 226—227).—The effect of 32 metallic catalysts on the decomp. of COS by $H_2SO_4$ at temp. up to 250° has been studied by measurement of the rate of formation of $SO_2$. Spongy Pd, Se, and Pt have the greatest effect, whilst the alkali metals and alkaline earths show a slight anticatalytic effect.
C. R. H.

**Active oxides. LXXXXV. Influence of various gases on the reaction between zinc oxide and chromium trioxide.** G. F. Hüttig, S. Cassirer, and E. Strotzer (Z. Elektrochem., 1936, **42**, 215—222).—The hygroscopicity and magnetic susceptibility of equimol. mixtures of ZnO and $Cr_2O_3$, which have been heated at various temp. up to 500° in vac., have been measured. With rise of temp., surface activity, as indicated by hygroscopic data, gives place to a period of inactivity which in turn is followed by activity due to internal diffusion. Finally, at about 400°, the activity is again reduced, which, with a rapid increase in the magnetic property, indicates the formation of cryst. $ZnCr_2O_4$. The influence of A, $NH_3$, $H_2O$, MeOH, $N_2O$, and air on the reaction has likewise been investigated.
C. R. H.

**Tin vanadate as a catalyst in the oxidation of toluene to benzoic acid.** R. Huitema and G. W. Brown (J. Physical Chem., 1936, **40**, 531—542).—The catalytic effect of Sn vanadate in the oxidation of PhMe to BzOH is affected by the extent to which it may have been previously heated. In the oxidation reaction, temp. and $[O_2]$ affect the ratio $CO_2$ : BzOH, but diluents, *e.g.*, $CO_2$ and $H_2O$, appear to have no effect. Anthraquinone and PhCHO are by-products.
M. S. B.

**Hydrogenation of carbonyl compounds by Raney nickel covered by metals of the platinum family. Influence of alkalis.** M. Delépine and A. Horeau (Compt. rend., 1936, **202**, 995—998; cf. this vol., 457).—The speed of hydrogenation (*v*) of COMeEt at room temp. and atm. pressure in presence of Ni is increased by depositing Pt group metals on the Ni. The efficiency of the added metals increases in the order Pd; Ru and Rh; Os, Ir, and Pt. Cu is without action, and Au has a small influence only. The addition of $Na_2CO_3$ solution increases *v*. Similar detailed results have been obtained with $CH_2Ac{\cdot}CO_2Et$, and the following hydrogenations have been effected on Pt+Ni: β-cholestanone → mainly dihydro*epi*cholesterol, furfuraldehyde → furyl alcohol, *d*- and *r*-pinonic acids → the corresponding alcoholic acids, *d*-, *l*-, and *r*-hydroxyketopinanes → dihydroxypinanes, and *d*-camphor → mainly *l*-*iso*borneol. With Ni and Ir *v* for CO*MeEt* is approx. const. above a small % of Ir, Pt, Ir, and Rh alloy with a small quantity of Ni, which remains with the Pt etc. after dissolving the catalyst in dil. HCl.
R. S. B.

**Amorphous and crystalline oxide hydrate and oxides. XXV. Formation of ozone and hydrogen peroxide from metallic peroxide compounds formed by the oxidation of metallic salts and metallic oxides with potassium persulphate.** A. Krause and G. Szmidt (Ber., 1936, **69**, [*B*], 805—811).—Co, $Ti^{IV}$, and $Zr^{IV}$ resemble $Fe^{III}$ in their ability to form $O_3$ and perheteropoly-acids in the system $K_2S_2O_8$–$H_2SO_4$. The apparent inability of other elements (*e.g.*, Ce, Cr, and U) to form similar acids may be due to their very marked catalytic ability to decompose $H_2O_2$ and $O_3$. An unexpectedly great "$O_3$ effect" is observed during the oxidation of Ag ferrite with $K_2S_2O_8$ in $0{\cdot}3N$-$H_2SO_4$. Simple Ag compounds ($Ag_2O$, $Ag_2SO_4$) also yield much $H_2O_2$ probably due to catalytic action associated with the formation of $Ag_2O_2$, its decomp., and re-formation. Under otherwise similar conditions metallic Ag gives solely $O_3$. Catalytic influences which accelerate the decomp. of $O_3$ and $H_2O_2$ are also observed in the systems.
H. W.

**Preparation of manganese catalysts for recovery of sulphur from hydrogen sulphide.**—See B., 1936, 452.

**Determination of the activity of contact catalysts for the sulphuric acid industry.**—See B., 1936, 406.

**Electrolytic oxidation and reduction of calcium cyanamide.** G. Calcagni and G. Lazzari (Annali Chim. Appl., 1936, **26**, 43—49).—$CaCN_2$, digested for approx. 12 days in 20% $H_2SO_4$ and then electrolysed (3 hr. at 5 amp. and 14 volts), yields $NH_3$ (up to 6·7% of the total N) at the cathode and $HNO_2$ (with some $HNO_3$) at the anode. F. O. H.

**Electrolysis of sodium nitrate in liquid ammonia.** E. I. Achumov, N. A. Gontscharov, and E. A. Ezerova (J. Gen. Chem. Russ., 1935, **5**, 1744—1753).—V.p. data are recorded for saturated solutions of $NaNO_3$ in liquid $NH_3$ at 0—30°, and conductivity data at −16° to 30°. During electrolysis the anode process is : $6NH_2' \rightarrow 4NH_3+N_2$ ; $NH_4^{\cdot}+NO_3' \rightleftharpoons NH_4NO_3$ ; $NH_4NO_3+NaNH_2 \rightarrow NaNO_3+2NH_3$, and the cathode process $Na+NH_3 \rightarrow NaNH_2+H$ ; $Na+H_2O \rightarrow NaOH+H$ ; $NaNH_2+H_2O \rightarrow NaOH+NH_3$. The process as a whole is represented by $6NaNO_3+14NH_3 \rightarrow 6NH_4NO_3+6NaNH_2+3H_2+N_2$. R. T.

**Electrolytic reductions of organic compounds at alloy cathodes. I. Reduction of aliphatic ketones to hydrocarbons at cadmium amalgams.** S. Swann, jun., H. J. Read, and F. C. Howard (Trans. Electrochem. Soc., 1936, **69**, Preprint 24).—The electrolytic reduction of $COMePr^{\alpha}$ to $n$-$C_5H_{12}$ has been studied at Cd–Hg cathodes containing 0—100% of Cd. When the yield is plotted against the composition of the amalgam, inflexions are obtained at points that correspond with phase changes in the amalgam. E. S. H.

**Transformation of a thin layer of copper sulphide under the influence of metallic copper is of an electrolytic nature.** H. Devaux (Compt. rend., 1926, **202**, 368—370 ; cf. this vol., 435).—When two strips of Cu foil are floated on aq. $CuSO_4$ and a film of CuS is formed between them, the development of a blue colour on the CuS begins at each foil and spreads from them with equal velocity. However, if a p.d. is applied between the foils it accelerates on the side of the negative electrode and becomes slower on the positive side. The colour change is attributed to deposition of Cu on the conducting CuS film. J. W. S.

**Mechanism of the electrolytic polishing of copper.** P. Jacquet (Compt. rend., 1936, **202**, 402—404 ; cf. this vol., 305, 571).—Factors favouring the diffusion of the products of attack (agitation, decreased acid concn., rise of temp.) raise the min. c.d. necessary for electrolytic polishing. During electrolysis a liquid zone is produced in contact with the anode of a thickness which is diminished by these factors and is of high resistance. This layer, being deeper in contact with grooves than opposite ridges, causes the latter to be first attacked. When $HPO_3$ is used as electrolyte this layer is first formed, but, contrary to the behaviour with $H_3PO_4$ and $H_4P_2O_7$, it later forms a solid crust. J. W. S.

**Anodic behaviour of organic salts of copper.** G. Kravtzov (Compt. rend., 1936, **202**, 1036—1038).—In the electrolysis of $CuSO_4$, $Cu(HCO_2)_2$, $Cu(OAc)_2$, and $Cu(EtCO_2)_2$ with Cu anodes the ratio *R* of the apparent loss of wt. of anode to the wt. of Cu deposited in a voltameter $=1$ or $<1$ corresponding with apparent valencies of 2 or 1—2. In the latter case $Cu_2O$ is deposited on the anode by hydrolysis of $Cu^I$ salts. Increase in c.d., and increase in dilution (except with salts of $HCO_2H$ and $EtCO_2H$) reduces the formation of $Cu^I$ salts. The time of electrolysis influences *R* considerably with many solutions, owing partly to the influence of $Cu^{\cdot\cdot}$ dissolved from the anode. The reactions $Cu \rightarrow Cu^{\cdot\cdot}$, $Cu \rightarrow Cu^{\cdot} \rightarrow Cu_2O$ occur, and are confirmed by a study of p.d.–time curves. R. S. B.

**Simultaneous electrodeposition of thallium and zinc.** W. G. Parks and I. M. Le Baron (Trans. Electrochem. Soc., 1936, **69**, Preprint 14, 171—182).—The electrolyte contains $TlClO_4$ and $Zn(NO_3)_2$ and is operated at c.d. 0·2—0·9 amp. per sq. dm. Unless the Tl content of the deposit is low oxidation is rapid. No serviceable plates were obtained. Only the eutectic cast and deposited alloys have similar structures. From cathodic potential measurements the composition of the deposit obtained at a given c.d. can be predicted. J. W. C.

**Electrolytic production of boron and its alloys.**—See B., 1936, 414.

**Alkaline plating baths containing ethanolamines. II. Nickel. III. Cobalt.**—See B., 1936, 458.

**Influence of composition of electrolyte in the electrolysis of carnallite.**—See B., 1936, 458.

**Electroplated gold.**—See B., 1936, 458.

**Synthesis of ammonia by cathodic sputtering of lead.** P. Jolibois and F. Olmer (Compt. rend., 1936, **202**, 1268—1269 ; cf. A., 1935, 1087).—The yield of $NH_3$ per watt dissipated increases with the pressure of the $N_2$–$H_2$ mixture. Prolonged cathodic action produces an equilibrium concn. of $NH_3$ corresponding closely with the thermodynamic val. at room temp. L. J. J.

**Formation of hydrogen peroxide in the electrodeless discharge in water vapour.** R. W. Campbell and W. H. Rodebush (J. Chem. Physics, 1936, **4**, 293).—When the dissociated $H_2O$ vapour is passed through a liquid-air trap, formation of $H_2O_2$ takes place exclusively in the latter. L. J. J.

**Constitution of mixed organo-magnesium compounds.**—See this vol., 743.

**Photochemical sensitivity of mercuric nitrate.** S. Schlivitch and D. Nikolitch (Bull. Soc. Chim. Yougoslav., 1935, **6**, 159—163).—The e.m.f. set up in a photogalvanic cell by illumination ($\lambda \not> 4600$ A.) of aq. $Hg(NO_3)_2$ is increased in presence of EtOH or glycerol. R. T.

**Photolysis of nitrates (spectrophotometric determination of potassium nitrate ; catalytic action of manganous salts).** H. Vogels (Bull. Acad. roy. Belg., 1936, [v], **22**, 320—333 ; cf. A., 1912, ii, 862).—The photochemical reduction of $KNO_3$ to $KNO_2$ in aq. solutions of varying $p_H$ has been studied, using the absorption at 3650 A. as a measure of $[KNO_2]$. The $p_H$ falls during the reaction, which does not lead to the establishment of the simple equilibrium $2KNO_3 \rightleftharpoons 2KNO_2+O_2$. The mechanism is discussed. The velocity increases considerably with change of $p_H$ from 7 to 10, but is little affected by further rise in $p_H$. The reaction is accelerated by $Mn^{II}$ salts and by tartrates. The effect with the former is not immediate, suggesting that the true catalyst is Mn in a higher state of oxidation.

D. R. D.

**Photographic photometry in the extreme ultra-violet.** (Mme.) R. Montagne and R. Ricard (Compt. rend., 1936, **202**, 477—479).—The factors of contrast for const. times of exposure and const. illumination respectively are const. within 10% over the range λ 2000—1250 A. for plates sensitised with Na salicylate. F. L. U.

**New process of development. Photo-electrochemical process.** K. M. Kosonogova (Compt. rend. Acad. Sci. U.R.S.S., 1936, **1**, 167—168).—A polished Cu electrode, covered with $Cu_2I_2$ by dipping in I in EtOH, is placed in $Pb(NO_3)_2$ solution and polarised at a potential about 0·3 volt < the normal electrode potential. At the illuminated parts, the electrode is covered with a greenish deposit. This can be strengthened by colouring with dyes, *e.g.*, rhodamine-*B*. A. J. M.

**Photochemical formation of ethylene iodide in solutions of carbon tetrachloride.** R. E. DeRight and E. O. Wiig (J. Amer. Chem. Soc., 1936, **58**, 693).—$C_2H_4I_2$ is formed when solutions of $C_2H_4$ and I in $CCl_4$ are exposed to red light. The rate of reaction depends on the pressure of $C_2H_4$ and decreases with decreasing [I]. No measurable dark reaction occurs. The mechanism is discussed. E. S. H.

**Photolysis of acetic acid.** M. Burton (J. Amer. Chem. Soc., 1936, **58**, 692).—Evidence for the formation of Me and at. H is given. E. S. H.

**Photobromination of acetylene dichloride in the gaseous state and in carbon tetrachloride solution.** J. C. Ghosh, S. K. Bhattacharyya, and S. C. Bhattacharyya (Z. physikal. Chem., 1936, **B**, **32**, 145—157).—The rate of reaction at 30° and 40° in light of λλ 546, 436, and 406 mμ has been determined. In both reactions the unimol. velocity coeff. in respect of $[Br_2]$, *k*, ∝ the square root of the energy absorbed, the temp. coeff. is 1·4, and the graph of $1/k$ against $1/\text{mean } [C_2H_2Cl_2]$ is rectilinear. Reaction in the gaseous state is about 30 times as rapid as in solution. These results agree with the mechanism previously suggested (A., 1930, 1260). The concn. of Br atoms in the stationary state and the velocity coeff. and activation energy of $Br + Br_2 \rightarrow Br_3$ have been calc.; apparently there is a steric factor of $\sim 10^{-2}$. Quantum yields have been determined. R. C.

**Addition of bromine and iodine to compounds with an ethylene linking. Photobromination of ethyl *m*-nitrobenzylidenemalonate, bromination of fumaric and maleic acids, addition of iodine to allyl alcohol.** A. Berthoud and M. Mosset (J. Chim. phys., 1936, **33**, 272—305).—The photobromination of Et *m*-nitrobenzylidenemalonate in $CCl_4$ is similar to that of cinnamic acid or stilbene (A., 1927, 528). The bromination of maleic (I) and fumaric (II) acids is not influenced by light and is more rapid for the ions than for the undissociated mols. $Br_2$ reacts more rapidly than $Br_3'$ on (I), but the opposite is the case for (II). The addition of I to allyl alcohol in $H_2O$ is also uninfluenced by light, but the action is reversible. In $CCl_4$ solution, however, there is a light reaction similar to photobromination. In the dark a reaction appears to take place mainly through the agency of $HI_5$. HI acts as an accelerator. M. S. B.

**Photo-oxidation of succinic acid by methylene-blue sensitised by uranyl salts.** J. C. Ghosh, T. Banerjee, and B. Bhatta (Z. physikal. Chem., 1936, **B**, **32**, 163—167).—In light of λ 366 mμ the reaction is, after an initial period of induction, of zero order in respect of methylene-blue. The velocity coeff., *k*, ∝ the intensity of incident radiation but is independent of the $p_H$, and the graph of $1/k$ against 1/succinic acid (I) concn. is rectilinear. Only half the collisions between the excited $UO_2^{\cdot\cdot}$ ion and the (I) mol. are effective. R. C.

**Photochemical oxidation of mandelic acid by bromine with uranyl salts as ultra-violet sensitisers.** J. C. Ghosh and B. B. Roy (Z. physikal. Chem., 1936, **B**, **32**, 158—162).—Below 313 mμ this is purely a sensitised reaction and unimol. in respect of $Br_2$. The velocity coeff., *k*, ∝ the square root of the incident energy and ∝ the square root of the energy absorbed by the $UO_2SO_4$ and a graph of $1/k$ against 1/mandelic acid concn. is rectilinear. The quantum yield is large. These results are accounted for by assuming that each quantum absorbed by the $UO_2^{\cdot\cdot}$ ion resolves a $Br_2$ mol. into atoms which then set up chains of the type previously suggested (A., 1930, 1260). R. C.

**Radiochemical synthesis and decomposition of hydrogen bromide.** S. C. Lind and R. Livingston (J. Amer. Chem. Soc., 1936, **58**, 612—617).—The reaction rate under the influence of Rn has been determined at 25° by measuring the pressure of $H_2$ when the reaction vessel was immersed in liquid $O_2$. A theory of reaction, which is consistent with the data, has been developed, and a relation between the ion pair yield and the initial pressures deduced.

E. S. H.

**Action of α-particles on mixtures of nitrogen and oxygen.** R. Cloetens (Bull. Soc. chim. Belg., 1936, **45**, 97—112).—Measurements of the changes with time of the pressure *p* of $Rn\text{–}O_2\text{–}N_2$ mixtures indicate that an initial diminution of *p* takes place at a rate which is a function of the concn. of the constituents of the mixture. A rapid increase in *p* follows and then a final slow decrease. The results are discussed on the basis of ionic yields calc. on the assumption of gaseous reactions of the type $A + B \rightarrow AB$. M. S. B.

**Preparation of distilled water in a vacuum.** J. Thomann and A. Kälin (Pharm. Acta Helv., 1935, **10**, 96—101; Chem. Zentr., 1935, ii, 1212).—$H_2O$ distilled in vac. is not necessarily sterile, whereas $H_2O$ distilled at 100° is sterile. H. N. R.

**Reaction of formaldehyde with hydrogen peroxide in heavy water. Non-exchangeability of hydrogen atoms of formaldehyde.** K. Wirtz and K. F. Bonhoeffer (Z. physikal. Chem., 1936, B, 32, 108—112).—In the reaction of $CH_2O$ with $H_2O_2$ in $D_2O$ solution there is evolved no D but only H, which therefore originates entirely in the $CH_2O$. This result supports Wieland and Wingler's mechanism of the reaction (A., 1923, i, 650). None of the H atoms of $CH_2O$ is exchangeable for D in $D_2O$.

R. C.

**Effect of heavy water on the colour of hydrated salts.** J. Bell (Nature, 1936, **137**, 534).—Solutions of $CuSO_4$ in 99·5% $D_2O$ are less intensely coloured than solutions of equal concn. in $H_2O$. Solid $CuSO_4,5H_2O$ and $CuSO_4,5D_2O$ are readily distinguishable by the difference in tint.

L. S. T.

**Bis-8-hydroxyquinoline inner complex salt of bivalent silver.**—See this vol., 613.

**Fluoberyllates and their analogy with sulphates. IV. Double salts of rubidium and cæsium fluoberyllates. V. Double salts of thallous fluoberyllate.** N. Rây (Z. anorg. Chem., 1936, **227**, 32—36, 103—106; cf. A., 1932, 706).—IV. The following *salts* are described: $M^I{}_2BeF_4,M^{II}BeF_4,6H_2O$ ($M^I$=Rb, $M^{II}$=Co, Zn, Cu, Cd, $Fe^{II}$); $Cs_2BeF_4,NiBeF_4,6H_2O$.

V. The *salts* $Tl_2BeF_4,M^{II}BeF_4,6H_2O$ ($M^{II}$=Ni, Co, Cu, Zn, Cd) are described. The properties of all of the above are similar to those of the corresponding sulphates, and the mol. vols. are of the same order of magnitude.

F. L. U.

**Basic magnesium sulphatocarbonate.** (Mme.) L. Walter-Lévy (Compt. rend., 1936, **202**, 1074—1076).—Aq. $KHCO_3$ was added to aq. $MgSO_4$ at 70° and boiled, and the ppt. obtained up to 2 hr. examined by *X*-rays and chemical analysis. $4MgO,2CO_2,SO_3,7H_2O$ is deposited with $MgSO_4$ 2—5 mols. per litre.

R. S. B.

**Magnesium cyanamide.** A. Perret and R. Perrot (Compt. rend., 1936, **202**, 420—422).—$Mg(CN)_2$ changes slowly at 300° and rapidly above 600°, yielding $MgCN_2$, which is also obtained on heating $Mg_2Fe(CN)_6$. $Mg[N(CN)_2]_2$, when heated above 500°, also yields $MgCN_2$, which decomposes into its elements at about 750°. $MgCl_2$ reacts with NaCN at 400° in presence of reduced Fe, and at 500° is absence of catalyst, yielding $MgCN_2$. The relative instability of $MgCN_2$ compared with alkaline-earth cyanamides is attributed to the weakness of the Mg·N linking and the volatility of Mg.

J. W. S.

**Marginal effect in the dissolution of magnesium in aqueous organic acids.** J. V. Durdin and A. M. Markevitsch (J. Gen. Chem. Russ., 1935, 5, 1690—1695).—When a Mg plate with part of its surface protected with paraffin wax is immersed in aq. org. acids, the most intense corrosion is observed around the margin of the protected area; this effect is not observed in presence of EtOH, or using mineral acids. The effect is ascribed initially to adsorption of acid at the paraffin wax–metal–solution boundary, and in the latter stages to more intense stirring of the solution by $H_2$ bubbles in the cavity formed below the margin of the wax.

R. T.

**Decrease of a calcite crystal in an active isotropic medium; corrosion figures in dolomite.** L. Royer (Compt. rend., 1936, **202**, 429—431).—The action of *d*- and *l*-tartaric, *l*-malic, and *l*-aspartic acids on the $a^1$ (111) face of calcite or dolomite yields equilateral triangular planes, as with inactive acids, but on the $b^1$ (110) and $e^2$ $(2\bar{1}\bar{1})$ faces of calcite the active acids yield asymmetric corrosion planes, whilst with inactive acids they are symmetrical.

J. W. S.

**Conversion of strontium sulphate into carbonate.** G. Gallo (Annali Chim. Appl., 1936, **26**, 109—115).—The most favourable conditions for the conversion of pptd. $SrSO_4$ (I) and celestine (II) into $SrCO_3$, by means of $(NH_4)_2CO_3$ solution, are: (1) $\nless$ 5 parts $H_2O$ to 1 part (I) or (II); (2) temp. 40—50°; (3) $\ngtr$ 25% $(NH_4)_2SO_4$ in solution for (I) and $\ngtr$ 15% for (II); (4) slightly increased pressure; (5) amount of $(NH_4)_2CO_3$, just above theoretical. (I) is more easily convertible than (II). Yields were 98·5% and 96·39%, respectively.

L. A. O'N.

**Barium osmichloride.** F. Puche (Compt. rend., 1936, **202**, 1285—1286).—*$BaOsCl_6$*, prepared by the action of $Cl_2$ on Os and $BaCl_2$ at 350°, forms orange crystals sol. in $H_2O$ and EtOH, dissociating reversibly above 430°. Data are recorded for equilibrium dissociation pressures of $Cl_2$ at 719—947° abs.

L. J. J.

**Method of dissolving pitchblende for the preparation of radium standards.** V. H. Matula (Coll. Czech. Chem. Comm., 1936, 8, 178—184).—The pitchblende (I) is fused with $Na_2CO_3$ in a Pt crucible, the melt dissolved in HCl, and the $SiO_2$ separated. This is decomposed by HF and any residue dissolved in $HNO_3$. The method is applicable to all (I) and is superior to the acid decomp. The Boltwood coeff. applies in the case of old, unweathered, (I).

R. S.

**Exothermic transformations of aluminium oxide.** D. Avdalian (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 173—175).—When $Al_2O_3,3H_2O$ is dehydrated there is a distortion of the lattice, but no exothermic effect could be observed with the $Al_2O_3$ produced. Hence the effect is probably not concerned with distortion of the lattice, contrary to Parravano (A., 1928, 1190). $Al_2O_3$ obtained by pptg. an aq. solution of $Al(NO_3)_3$ with aq. $NH_3$, and by dehydrating $Al_2O_3,3H_2O$ are identical, and give an exothermic arrest at 850°, as does $Al_2O_3$ obtained by heating $AlCl_3,6H_2O$.

A. J. M.

**Separation of rare earths by chromatographic adsorption.** E. Lange and K. Nagel (Z. Elektrochem., 1936, 42, 210).—Theoretical.

F. L. U.

**Graphite formation. II. Chemical nature of graphite and amorphous carbon.** A. E. Balfour, H. L. Riley, and R. M. Robinson (J.C.S., 1936, 456—461).—Evidence for the chemical resemblance of graphite and the triarylmethyls is supported by the facts that the capacity of sugar charcoal to absorb $H_2$ decreases with temp. above 900° whilst the wet-oxidation rate (this vol., 178) increases and the sp. electrical resistance decreases. The wet oxidation of C free from H is very rapid. The graphitisation of coke is increased with the rapidity of carbonisation.

F. R. G.

**Reaction of carbonyl chloride with hexamethylenetetramine.** N. A. Pushin and R. D. Živadi-

NOVIĆ (Bull. Soc. Chim. Yougoslav., 1935, 6, 165—168).—$(CH_2)_6N_4$ and $COCl_2$ in $CHCl_3$ yield a 1 : 1 compound, m.p. 187—190°, decomposed by $H_2O$ to yield $CH_2O$, $NH_4Cl$, and $CO_2$. R. T.

**Silica fluff.** C. A. Jacobson (J. Physical Chem., 1936, 40, 413—418).—The product formed by drying slowly at room temp. hydrated $SiO_2$ obtained by the action of $SiF_4$ on $H_2O$ has *d* 1·018 and composition $12SiO_2,3H_2O$. The material in its usual state of packing has an apparent *d* 0·025 and can flow like a liquid through narrow tubes. Its chemical nature is discussed. F. L. U.

**Titanium. II. Decomposition of titanomagnetite concentrate with dilute sulphuric acid.** E. G. Schtandel (J. Gen. Chem. Russ., 1935, 5, 1629—1633).—The rate of dissolution in aq. $H_2SO_4$ of $Fe_2O_3$ in titanomagnetite is > that of $TiO_2$. In both cases it rises rapidly with increasing $[H_2SO_4]$ to 30%, and then continues to rise more slowly; it is greater at higher than at lower temp. R. T.

**Composition of titanium nitride.** E. A. Ostroumov (Z. anorg. Chem., 1936, 227, 37—42).—Ti nitrides, when heated in a stream of $Cl_2$, are completely converted into $TiCl_4$ below 300°, at which temp. neither $TiO_2$ nor lower oxides are perceptibly attacked. Examination of technical and laboratory Ti nitride preps. by this method showed a varying content of $TiO_2$. In two specimens the nitride fraction corresponded with $Ti_5N_6$, whilst the remainder appeared to contain a mixture of nitrides. F. L. U.

**Lead complexes of hydroxy-acids.**—See this vol., 706.

**Preparation of pure $N_2O_4$.** A. V. Toptschiev (J. Gen. Chem. Russ., 1935, 5, 1718—1722).—$H_2SO_4$ is added to saturated aq. $NaNO_2$, and sufficient $O_2$ is mixed with the gases to convert NO into $NO_2$. No advantage is gained by using $V_2O_5$ catalyst at 20—200°, and higher yields of $N_2O_4$ are obtained at low than at high temp. R. T.

**Preparation and b.p. of phosphorus trichloride.** I. Teodoreanu (Bull. Acad. Sci. Roumaine, 1935, 17, 38—40).—An apparatus for the prep. of pure $PCl_3$ is described. The b.p. is 75·5—76°/749—755·9 mm. R. S. B.

**Hydrolysis of phosphorus dichloronitrides and their amines.** A. M. de Ficquelmont (Compt. rend., 1936, 202, 423—425; cf. this vol., 566).—Treatment of an $Et_2O$ solution of $P_3N_3Cl_4(NH_2)_2$ (I) with NaOAc solution yields $P_3N_2O_8H_4Na_3$ (II). The slowness of hydrolysis of (I) suggests a difference in its mechanism from the hydrolysis of the trimeric and tetrameric chlorohydrins, probably owing to the solidity of the linking of the $NH_2$-groups. This makes it improbable that $P_4N_4O_8H_8$ is an intermediate product in the formation of (II). $P_4N_4O_8H_8$ yields very little $P_3N_2O_8H_7$ on hydrolysis. J. W. S.

**Double decomposition in solution of sodium niobates with metal salts.** P. Süe (Compt. rend., 1936, 202, 486—488; cf. A., 1935, 825).—Conductometric titration of various metal salts with $Na_2O,Nb_2O_5,7H_2O$ (I) and $7Na_2O,6Nb_2O_5,32H_2O$ (II) indicates the formation of corresponding niobates as follows: with (I), Ca, Sr, Ba, Ag, Cu, $Hg^I$, Tl, Zn, Cd, Co, Ni, Mn, Pb; with (II), Ag, Tl, Mg, Ca, Sr, Ba. F. L. U.

**Etherates of iodobismuthous and iodoantimonious acids.** V. Auger and (Mlle.) N. Ivanov (Compt. rend., 1936, 202, 484—486).—The following *compounds* are described: $HBiI_4,16H_2O,10Et_2O$; $HSbI_4,5H_2O$ (yellow prisms); $HSbI_4,11H_2O,13Et_2O$. F. L. U.

**Amphoteric hydrated oxides, solutions of their hydrolysing salts, and their high-molecular compounds. XXXI. Hydrolysis and properties of bismuth perchlorate.** M. Prytz and P. Nagel (Z. anorg. Chem., 1936, 227, 65—80; cf. A., 1935, 181, 703).—Conductometric, potentiometric, and thermometric titrations, and measurements of diffusion and of optical absorption, indicate that $Bi(ClO_4)_3$ is stable only in presence of very conc. $HClO_4$ when the solution is 0·1*M* with respect to Bi. With $HClO_4 : BiO{\cdot}OH = 6{\cdot}5$ hydrolysis to $BiOH(ClO_4)_2$ is complete. With decreasing $[HClO_4]$ further hydrolysis to $(BiOH)_2O(ClO_4)_2$ occurs, accompanied by condensation which, at $HClO_4 : BiO{\cdot}OH < 2{\cdot}5$, yields $(BiOH)_4O_3(ClO_4)_2$. The *compounds* $Bi_3O_2(OH)_3(ClO_4)_2$ and $Bi_2O_2(OH)ClO_4$ (bimol. in solution) have been prepared and analysed. Their solubility in $H_2O$ is about 0·025 mol. per litre, in contrast to the readily sol. $BiOClO_4$. F. L. U.

**Hydrolysis of protoactinium and its reaction with sodium thiosulphate in acid solutions.** Cheng Da-Chang and H. Li (J. Chinese Chem. Soc., 1936, 4, 93—97).—When acid solutions of active $TiO_2$ are treated with $Na_2S_2O_3$ in the presence of $(NH_4)_2MoO_4$ or a Cu salt, some Pa is pptd. with the $MoS_3$ or CuS. In slightly acid solutions hydrolysis occurs and Pa is pptd. with the Ti, little Pa being pptd. with the sulphide. C. R. H.

**Entrainment of protoactinium by titanium and a method of purification.** (Mme.) Emmanuel-Zavizziano (Compt. rend., 1936, 202, 1052—1054).—In the chemical purification of ppt. of active Ti, Sn is only partly eliminated from a mixture of Ti, Sn, Bi, Pb, and Pa hydroxides by NaOH, but on treating the mixed hydroxides with yellow $(NH_4)_2S$, Ti and Pa remain as hydroxides, Sn forms a sol. polysulphide, and Bi and Pb form insol. sulphides. Treatment of the residue with dil. HF dissolves the hydroxides of Ti and Pa (with radioactive impurities). For radioactive purification, 1 c.c. of conc. $H_2SO_4$ is added to the HF solution, HF is evaporated off, and $H_2O$ and aq. $NH_3$ are added. The hydroxides are then dissolved in HCl and a few drops of 1% nitrates of La, Bi, Th, Pb, and Ba are added. The whole is pptd. hot by aq. $NH_3$, and the ppt. is washed with 2% $(NH_4)_2SO_4$ to remove all $NH_3$, since this gives with HF double fluorides of Pa and $NH_4$ and of Ti and $NH_4$ which are incompletely pptd. by $NH_3$. The hydroxides of Pa and Ta alone dissolve in HF. The whole is repeated 3 or 4 times. For the concn. of Pa, a few drops of $H_2O_2$ are added to the dil. solution in $H_2SO_4$, which is then heated just to boiling. A part of the Ti is pptd. as $TiO_2$ and entrains a proportion of Pa which varies with the concn. of acid, the % of $H_2O_2$, and the temp. R. S. B.

**Thiosulphato-compounds. I.** H. BRINTZINGER and W. ECKARDT (Z. anorg. Chem., 1936, **227**, 107—111).—Dialysis coeffs. of complex ions formed from salts of various heavy metals and $Na_2S_2O_3$ have been measured at 18°. The calc. ionic wts. indicate the existence of the following ($S_2O_3=X$): $[Ag_2X_2]''$; $[Cu_2X_2]''$; $[Tl_2X_2]''$; $[M^{II}X_3]''''$ ($M^{II}$=Mn, Fe, Co, Ni, Zn, Cd). F. L. U.

**Molybdenum blues.** V. AUGER (Compt. rend., 1936, **202**, 1180—1182).—The unstable Mo blue obtained by dissolution of $MoO_3$ in conc. $H_2SO_4$ can form stable blue complexes with alcohols, $COMe_2$, and AcOH. The stable *complex* with AcOH has been isolated and analysed. Its composition appears to be $Mo_2O_5,4MoO_3,SO_3,4AcOH,4H_2O$. $SO_3$ is not in a form precipitable by $BaCl_2$. M. S. B.

**Polarimetric study of the formation of complex molybdosaccharates.** H. PARISELLE and F. CHIRVANI (Compt. rend., 1936, **202**, 482—484; cf. A., 1934, 252, 992).—Polarimetric observations of K or $NH_4$ molybdates with saccharic acid ($SaH_2$) or $SaK_2$ in aq. solution indicate the existence of the compounds $3SaH_2,7MoO_3,3(K,NH_4)_2O$, $M[\alpha]$ $-70°$; and $3SaH(K,NH_4),7MoO_3,3(K,NH_4)_2O$, $M[\alpha]$ $+1050°$.
F. L. U.

**Preparation of hydrofluoric acid.** A. BOOKHEIM (J. Chem. Educ., 1936, **13**, 93). L. S. T.

**Chrétien's iodine sulphate.** F. FICHTER and A. DINGER (Helv. Chim. Acta, 1936, **19**, 607—608).—Chrétien's formula, $I_2O_3,SO_3,0{\cdot}5H_2O$ (A., 1897, ii, 138), is confirmed, but not that of Bahl *et al.*, $I_2O_3,H_2SO_4$ (A., 1935, 1335). Further, the compound $I_2O_4,H_2SO_4$, described by the latter, was probably simply $I_2O_3,SO_3,0{\cdot}5H_2O$ partly decomposed by $H_2O$.
M. S. B.

**Anionic iron.** R. SCHOLDER [with H. WEBER, CHRISTOPH, and DOLGE] (Angew. Chem., 1936, **49**, 255—259).—By the action of boiling aq. NaOH on reduced Fe in the absence of $O_2$, Fe is dissolved as $Fe^{II}$, with the simultaneous evolution of 2 atoms of H per atom of Fe dissolved, up to a limiting concn. which is a max. with 55% NaOH. With massive Fe, action is similar but proceeds less far. The limiting concn. of Fe is conditioned by electrochemical considerations, and in glass vessels is > in Fe or Ag, due to formation of silicato-ferroates from dissolved $SiO_2$. From the blue alkaline solution the *ferroate* $FeO,Na_2O,2H_2O$ (I) or $Na_2[Fe(OH)_4]$ is deposited on cooling, and with $Ba(OH)_2$ or $Sr(OH)_2$ gives $FeO,2(Ba,Sr)O,3H_2O$ or $(Ba,Sr)_2[Fe(OH)_6]$, in conformity with the hydroxo-salts of Zn, Co, and Cu. Addition of $H_2O$ ppts. $Fe(OH)_2$. Atm. oxidation of the solution of (I) at 20—25° gives the *ferrite* $Na_5[Fe(OH)_8],5$—$6H_2O$, and at 30—70° gives $Na_4[Fe(OH)_7H_2O)],1$—$2H_2O$. The 50% NaOH solution of (I) at 100—125° yields an olive-green *meta-ferrite*, $NaFeO_2$ (II), isomeric or polymeric with the red $NaFeO_2$ (III) prepared by the action of $Fe_2O_3$ on fused NaOH. (III) is formed also by the oxidation of boiling 55—60% NaOH solutions of (I), and differs from (II) in being stable to dil. NaOH. $Na_2S$ gives with solutions of (I) green solutions depositing the *thiohydroxoferroate* $Na_3[S{:}Fe(OH)_3],2H_2O$. Ferrite solutions similarly give $Na_8[(H_2O)(HO)_6Fe{\cdot}S{\cdot}Fe(OH)_6(H_2O)],2H_2O$. Under no conditions was $K_2FeO_5$ formed (cf. A., 1927, 433), and its existence is improbable. J. S. A.

**Autoxidation of iron, manganese, and cobalt hydroxides.** J. HERMAN (Compt. rend., 1936, **202**, 419—420; cf. A., 1935, 834).—The amount of $O_2$ absorbed by $Fe(OH)_2$ pptd. by KOH from excess of $FeSO_4$ in an atm. of $O_2$ increases with time to attain a limiting val. in 2 min. This amount is > that corresponding with transformation into $Fe^{III}$. With $MnSO_4$ there is a rapid initial absorption, followed by slow reaction ∝ time, attaining a limit corresponding, approx., with the conversion into $Mn^{III}$. If excess of KOH is present, however, this state is passed. With excess of $CoSO_4$ a green ppt. is obtained which is almost non-oxidisable under the conditions investigated. The same results are obtained with the respective chlorides. J. W. S.

**Action of anhydrous ferric chloride on anhydrous acetic and formic acids.** H. FUNK and M. DEMMEL (Z. anorg. Chem., 1936, **227**, 94—102; cf. A., 1931, 1020).—Interaction of anhyd. $FeCl_3$ and anhyd. AcOH yields the *compound* $[Fe_3(OAc)_6]Cl_3,AcOH$ (I), in which the AcOH is directly replaceable by $Et_2O$. (I) reacts with EtOH, MeOH, $COMe_2$, and dioxan to give the following *compounds* ($[Fe_3(OAc)_5OH]Cl_3=Z$): $Z,4EtOH$; $Z,4MeOH$; $Z,1{\cdot}5COMe_2$; $Z,4C_4H_8O_2$; $Z,2C_4H_8O_2$. $FeCl_3$ with $HCO_2H$ (95%) gives $Fe(HCO_2)_2Cl,H_2O$, which is also obtained with anhyd. $HCO_2H$, CO being evolved in the latter case. The product could not be dehydrated. F. L. U.

**Reaction of ferric salts with organic acids.** A. ZAIDES (J. Gen. Chem. Russ., 1935, **5**, 1530—1536).—$Fe(OH)_3$ does not react chemically with AcOH or $HCO_2H$, the only effect being that of peptisation of the gel. With $H_2C_2O_4$ a complex, probably $Fe[Fe(C_2O_4)_3]$, is formed. R. T.

**Amorphous and crystalline oxide hydrates and oxides. XXIV. Autoxidation and induction actions of ferrous hydroxide in presence of $\gamma$-FeO·OH.** A. KRAUSE and Z. ERNST (Ber., 1936, **69**, [*B*], 656—664; cf. A., 1935, 1335).—The action of air on an undisturbed ammoniacal mixture of $Fe(OH)_2$ and $\gamma$-FeO·OH causes oxidation of $Fe(OH)_2$ and ferro-ferrite reaction which may interfere with one another. The relative rates of the two reactions govern the processes occurring in the system, $Fe(OH)_2$–$\gamma$-FeO·OH. During autoxidation $Fe(OH)_2$ behaves as inductor and acceptor, the activating no. being about 2. Higher vals. are explained by the hypothesis that the double $O_2$ excess absorbed by 2 mols. of $Fe(OH)_2$ cannot oxidise the 2 additional $Fe(OH)_2$ mols. which have previously combined with $\gamma$-FeO·OH to produce the black ferro-ferrite; the latter is stable towards atm. oxidation. The chemistry of the process is complex and may be considered as a chain reaction. $H_2O_2$ is produced. In presence of EtOH as acceptor the activation no. is about 3. If ferro-ferrite reaction does not occur in the system $Fe(OH)_2$–$\gamma$-FeO·OH [as when $Fe(OH)_2$ is rapidly oxidised], the activation no. is about 1 or 1·4 or 2 with EtOH and $NaAsO_3$, respectively, as acceptor. In such cases $\gamma$-FeO·OH is without influence. H. W.

**Basic salts. XII Chemistry and morphology of basic salts of bivalent metals. IV. Basic cobalt bromides.** W. Feitknecht and G. Fischer (Helv. Chim. Acta, 1936, 19, 448—466; cf. A., 1935, 716).—Four *basic* $Co^{II}$ *bromides* exist. The green basic bromide I is pptd. at room temp., as a disperse gel, from aq. $CoBr_2$ of concn. 1·5—approx. $3·5\times10^{-2}M$ by $<$ the equiv. quantity of NaOH. At 100° the upper limit falls to $0·5M$. The ppt. becomes micro-cryst. by slow hydrolysis at higher temp. It is probably metastable only under all conditions. After long ageing or slow hydrolysis the compound contains more $Co(OH)_2$ than corresponds with the formula $CoBr_2,9Co(OH)_2$. The initial ppt. contains 7—11 $Co(OH)_2$ to each $CoBr_2$, according to the end concn. of the solution. From data relating to this compound the solubility product of $Co(OH)_2$ is $3·3\times10^{-15}$. Basic bromide II, $CoBr_2,3Co(OH)_2$, is reddish-violet and coarsely cryst., the form changing with the temp. of separation, which must be above room temp. It is stable towards $H_2O$. Basic bromide III is formed, not very readily, as dark bluish-violet crystals of unknown composition, by warming I in $3·5\times10^{-2}$—$0·1M$-$CoBr_2$. I, II, and III give characteristic $X$-ray diagrams. A rose-coloured basic bromide IV is obtained as a partly amorphous product by heating bromide I in a sealed tube above 150° in dil. aq. $CoBr_2$. A mixed basic chloride-bromide, isomorphous with basic chloride II, and of composition $CoCl_{1·34}Br_{0·66},3Co(OH)_2$, has also been obtained. M. S. B.

**Complex salts of dipyridyl with bivalent and tervalent cobalt.** F. M. Jaeger and J. A. van Dijk (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 164—175; cf. A., 1935, 714).—Analyses and crystallographic data for the following complex *salts* are given: $[Co(dipy)_3]Cl_2,6H_2O$; $[Co(dipy)Cl_2]5H_2O$; $[Co(dipy)_2(H_2O)_2]Cl_2,4H_2O$; $[Co(dipy)_2CO_3]Cl,2H_2O$; $[Co(dipy)_3]SO_4,7H_2O$; $[Co(dipy)(H_2O)_2]SO_4,4H_2O$; $[Co(dipy)_2CO_3]_2SO_4,9H_2O$; $[Co(dipy)_3](NO_3)_2,6H_2O$; $[Co(dipy)_2CO_3]NO_3,5H_2O$; $[Co(dipy)_2Cl_2]Cl,2H_2O$; $[Co(dipy)_3]_2(SO_4)_3,5H_2O$; $[Co(dipy)_3]Cl_3,3H_2O$. O. J. W.

**Hydrolysis of basic nickel sulphate.** G. Gire (Compt. rend., 1936, 202, 1182—1184).—$H_2O$ gradually reacts with the compound $5NiO,SO_3,nH_2O$ (I) previously obtained (A., 1935, 716), dissolving $NiSO_4$ and forming insol. $Ni(OH)_2$. There are no indications of the existence of any salt more basic than (I). M. S. B.

**Oxyhalides of nickel obtained by Sénarmont's synthesis.** A. Ferrari and R. Curti (Gazzetta, 1936, 66, 104—114).—When $CaCO_3$ is heated with aq. $CoCl_2$ in a sealed tube $CoCO_3$ is formed. With $NiCl_2$ no $NiCO_3$, but the compound $3Ni(OH)_2,NiCl_2$ (I), is formed. This substance is hexagonal, and on further heating with $NiCl_2$ gives the compound $Ni(OH)_2,NiCl_2$. A compound analogous to (I) can be obtained by using $NiBr_2$. These substances are probably solid solutions. O. J. W.

**Complex compounds of semicarbazides.** K. A. Jensen and E. Rancke-Madsen (Z. anorg. Chem., 1936, 227, 25—31; cf. A., 1934, 1188).—The following *compounds* of semicarbazide (=sem) and its derivatives are described: $[Ni\ sem_2]Cl_2$; $[Ni\ sem_2]SO_4$; $[Ni\ sem_3]Cl_2$; $[Co\ sem_3](NO_3)_2$; $[Ni(CON_3H_4)_2]$; $[Cu(NHAc\cdot NH_2)_2]SO_4$; $[Ni(NHAc\cdot NH_2]_3]SO_4$; $[Ni(EtO\cdot CO\cdot NH\cdot NH_2)_3]SO_4$; $[Ni(NHPh\cdot CO\cdot NH\cdot NH_2)_3](NO_3)_2$; $[Cu(NHPh\cdot CO\cdot NH\cdot NH_2)_2](NO_3)_2$; $[Ni(NH{:}C(O\cdot)\cdot NMe\cdot NH_2)_2]$; $[Ni(NH{:}C(O\cdot)\cdot NMe\cdot NHMe)_2,NH_2\cdot CO\cdot NMe\cdot NHMe]$; $[Cu(NH_2\cdot CO\cdot NMe\cdot NHMe)_2]SO_4$; $[Ni(NHPh\cdot CS\cdot NMe\cdot NHMe)_2]Cl_2$. F. L. U.

**Osmic acid esters as intermediate products in oxidations.**—See this vol., 603.

**Quantitative spectral analysis.** W. van Tongeren (Chem. Weekblad, 1936, 33, 249).—A correction (cf. this vol., 441). S. C.

**Spark and arc spectrum of pure iron as accessory for qualitative emission spectrum analysis. Iron alloys.** H. Hammerschmid, C. F. Linström, and G. Scheibe (Mitt. Forsch. Anst. Konz. Gutehoffnungshütte, 1935, 3, 223—229; Chem. Zentr., 1935, ii, 1221—1222).—Procedure and sensitive lines for the detection of the elements commonly alloyed with or present in Fe are recorded. J. S. A.

**Theory of titration error.** S. Kilpi (Z. anal. Chem., 1936, 104, 390—400).—Expressions are developed for the calculation of titration errors in those acidimetric and pptn. analyses in which the end-point does not coincide with the true equivalence point. J. S. A.

**Application of polarographic method in analytical chemistry. I. Theoretical introduction.** H. J. Antweiler (Z. anal. Chem., 1935, 102, 385—393).—The principles of the method are reviewed, and modified apparatus is described. J. S. A.

**Titrimetric colorimetry.** P. Karsten (Pharm. Weekblad, 1935, 72, 1327—1339).—The method of varying the thickness of a standard solution is untrustworthy, since Beer's law is rarely applicable, and that of preparing a series of standards is tedious and less accurate than the method recommended, viz.: equal quantities of the reagent are placed in two similar Nessler glasses; to one is added a known vol. of the solution to be analysed, whilst to the other a standard solution of the substance to be determined is added from a burette until the colours match. For determining $Fe^{III}$, 50 c.c. of the reagent (I) should contain 2·5 c.c. of $4N$-$HNO_3$ and 5 c.c. of $N$-KCNS, the suitable concn. (II) of Fe being 0·04—0·10 mg. in 50 c.c. of solution, the thickness of which is 10 cm.; substances which interfere (III) are Bi, Co, $Hg^{II}$, $Cu^{II}$, Ag, Ni, oxalate, phosphate, and alkali and alkaline-earth sulphates, chlorides, and nitrates. Corresponding data for other determinations are: CNS′ determination: (I) 2 c.c. $4N$-$HNO_3$ and 0·5 c.c. $N$-$FeCl_3$; (II) 0·15—0·40 mg. Bi determination: (I) 2·5 c.c. $4N$-$HNO_3$ or -$H_2SO_4$, 5 c.c. 20% KI, 6 drops 1% $NaHSO_3$; (II) 0·05—0·15 mg.; (III) Cu, Pb, Sb, Ag, Fe, Cl′. Cu determination: $NH_3$ method—(I) 5 c.c. 10% $NH_3$; (II) 0·5—3·0 mg.; (III) Bi, Co, Ni, Cr, Fe; $Fe(CN)_6''''$ method—(I) 1 c.c. 10% AcOH, 1 c.c. $N$-$NaHCO_3$, 2—3 drops 1% $K_4Fe(CN)_6$, 1 c.c. 10% $NH_4Cl$; (II) 0·15—0·30 mg.; (III) Zn, Hg, Co, Cr, Fe; Na diethyldithiocarbamate (IV) method—0·5 c.c. 10% $NH_3$, 1 c.c. 1% gum arabic, 5 c.c. 0·1% (IV); (II) 0·01—0·05 mg.; (III) Pb, Zn, Al, Bi, Hg, Cr, Ag, Sb, Sn, Mn, Ni, Co, Fe; $Na_2S$ method—(I) 1 c.c. 10% AcOH, 1 drop 10% $Na_2S$ in glycerol, 1 g. $NH_4Cl$; (II) 0·03—0·10 mg.; (III) Pb, Zn, Hg, Bi, Cd, Ni, Co, Sn, Sb, As, Fe; in presence of Pb, 2 c.c. $4N$-$H_2SO_4$ may be used in place of the AcOH. Pb determination with $Na_2S$ as in the case of Cu (with AcOH)—(II) 0·8—0·20 mg. (*sic*); (III) Cu, Zn, Hg, Bi, Cd, Ni, Co, Sn, Sb, As, Fe—or in alkaline solution: (I) 2·5 c.c. 10% $NH_3$, 1 drop 10% $Na_2S$ in glycerol, 1 g. $NH_4Cl$; (II) 0·05—0·10 mg.; (III) Fe, Hg, Bi, Cd, Co, Mn, Cr, Sb, Sn; if Ni, Ag, Cu, or Zn is present, KCN must be added. Cr determination: diphenylcarbazide (V) method—to the solution containing Cr $4N$-$HNO_3$ is added until the acidity reaches 1·0—1·5$N$, followed by 1 c.c. 0·1$N$-$AgNO_3$ and 1 g. $NH_4SO_4$. The solution is boiled for 3 min., cooled, and poured into the Nessler glass. 0·5 c.c. of (V) solution, containing 2 g. of (V) dissolved in 10 c.c. of glacial AcOH and diluted to 100 c.c. with 96% EtOH, are finally added; (II) 0·003—0·010 mg.; (III) Mn [reduce $MnO_4'$ with $H_2C_2O_4$ before adding (V)], Fe, Cl′. If the $CrO_4''$ is determined directly, without adding (V), (II) is 1·4 mg. Mn determination: boil for 5 min. with either 5 c.c. 50% $H_2SO_4$, 1 c.c. 0·1$N$-$AgNO_3$, and 0·5 g. $NH_4SO_4$, or 2—3 c.c. 85% $H_3PO_4$ and 0·25% periodate; (II) 0·06—0·16 mg.; (III) Cr, Cl′ (in first case). Phenolphthalein determination: (I) 1 c.c. 0·1$N$-NaOH; (II) 0·02—0·07 mg. Salicylic acid determination: (I) 2 c.c. $FeCl_3$ solution containing 54 mg. $FeCl_3,6H_2O$ and 10 c.c. glacial AcOH diluted to 100 c.c. with $H_2O$; (II) 0·15—0·25 mg.; (III) benzoic, cinnamic, tartaric, oxalic, and phosphoric acids and their salts, HCl, $HNO_3$, $H_2SO_4$, NaOH, and $Na_2CO_3$. Adrenaline determination: (I) 1 c.c. 10% $(NH_4)_2MoO_4$; (II) 0·5—2·0 mg.; (III) other pyrocatechol derivatives. Fe may be removed with $Na_4P_2O_7$. D. R. D.

**Ebulliometric determination of small amounts of water.** M. Wojciechowski (Nature, 1936, **137**, 707).—The sensitivity of the method is markedly increased by using the azeotropic mixture $Pr^aOH$–PhMe instead of EtOH–$C_6H_6$. L. S. T.

**Hydrogen peroxide reaction with diphenylcarbazide.** L. N. Lapin (Z. anal. Chem., 1935, **102**, 418—420).—$K_2Cr_2O_7$ is added to the acidified solution, forming perchromic acid (I) which is extracted with $Et_2O$ (peroxide-free). The (I) in the $Et_2O$ layer formed from 0·005 mg. of $H_2O_2$ gives a violet coloration with an EtOH–$Et_2O$ solution of diphenylcarbazide (II). Alternatively, Br may be added to the acidified test solution to oxidise $Fe^{II}$, S″, etc., followed by 2 c.c. of 0·00002$N$-$K_2CrO_4$. Free Br is removed by adding PhOH. On adding (II), no violet coloration or a weakened colour is obtained in presence of $H_2O_2$, due to the formation of (I), and its rapid decomp. to $Cr^{III}$. The method may be used to determine minute amounts of $H_2O_2$. J. S. A.

**Micro-determination of chlorine.** I. M. Korenman (Mikrochem., 1936, **19**, 144—146).—Free Cl in $H_2O$ is titrated with aq. Me-red or, better, with 0·001$M$-Me-orange. J. S. A.

**Nephelometric micro-determination of chlorine and its application to determination of chlorine in [ash of] organic substances.** F. Alten and E. Hille (Mikrochem., 1936, **19**, 118—128).—Stable AgCl sols are formed by the addition of Cl′ to a solution of 0·01$N$-$AgNO_3$+0·05$N$-$Al(NO_3)_3$+0·05$N$-$Ca(NO_3)_2$+0·1$N$-$NaNO_3$. The turbidity formed may be measured photometrically, and is ∝ Cl′. The method is applicable to 0—0·25 mg. of Cl. Org. materials (plant tissue etc.) are ashed, with the addition of lactose+$Na_2O_2$. The residue is dissolved in $H_2O$, and treated with 10% $H_2SO_4$ at 70—80° to destroy CN′. Cl in the filtered solution is then determined as above. J. S. A.

**Determination of hydrobromic acid in presence of hydrochloric acid.** G. G. Longinescu and E. I. Prundeanu (Bull. Acad. Sci. Roumaine, 1935, **17**, 47—51).—The solution containing Cl′ and Br′ is shaken with $H_2O_2$, $H_2SO_4$, and petrol, when the Br liberated by the $H_2O_2$ is absorbed by the petrol. HCl remains in the aq. layer and can be determined as AgCl. The petrol layer is reduced by Na and $C_5H_{11}$·OH and the Br determined as AgBr, volatilisation on heating being avoided. Results are accurate to 0·06%. R. S. B.

**Separation of bromides from chlorides by means of iodic acid.** L. Martini (Annali Chim. Appl., 1936, **26**, 102—105).—Kolthoff's modification of Bugarszky's method (Z. anal. Chem., 1921, **60**, 405) gives satisfactory results in the presence of a limited amount of Cl′ if the Br content is $\nless$ 7—8 mg. L. A. O'N.

**Reactions occurring during the absorption of nitrous vapours by potassium iodide solutions.** M. Dodé (Compt. rend., 1936, **202**, 1076—1078; cf. this vol., 439).—The action of $NO_2$ on aq. KI is expressed by: $N_2O_4+2KI=2KNO_2+2I$ (1); $N_2O_4+H_2O=HNO_2+HNO_3$ (2); $HNO_2+KI=NO+KOH+I$ (3); $HNO_3+KOH=KNO_3+H_2O$ (4); $2N_2O_3+2H_2O=4HNO_2$, $4HNO_2+2KI=2KNO_2+2NO+2I+2H_2O$ (5). In presence of $O_2$ the NO liberated in (3) is oxidised in the gas phase when the vol. of solution is small, or otherwise directly to $HNO_2$ in solution. The indirect production of nitrite by (5) increases with the dilution. The difference in hydrolysis of $NO_2$ and NOCl may be explained. $N_2O_4$ is equiv. to 2I, as may be proved: (*a*) in the titration of I by $Na_2S_2O_3$ in presence of nitrites; I consumed by oxidation of $NaNO_2$ is entirely regenerated by $NaNO_2+2HI=NaI+H_2O+I+NO$, $NO+\frac{1}{2}O_2+KI=KNO_2+I$ or $NO+O_2+KI=KNO_3+I$; (*b*) iodometric titration of acids by the action of the acid on a mixture of $KNO_2$ and KI in presence of $O_2$; (*c*) determination of $NO_2$ and $Cl_2$ in a mixture. Analytical application for the determination of nitrous vapours is discussed. R. S. B.

**Determination and detection of fluoride ion with lanthanum.** J. Fischer [with E. Müller and H. Knothe] (Z. anal. Chem., 1936, **104**, 344—346).—The determination of F by pptn. as $LaF_3$ (cf. A., 1925, ii, 598) is not practicable owing to the strong adsorptive properties of $LaF_3$. As a qual. test, by pptg. from AcOH solution in presence of dyes (*e.g.*, eosin) the dye is taken up, giving a red ppt. Limiting concn., 1 in 50,000. J. S. A.

**Determination of ozone and nitrogen peroxide in air.** G. A. Gorodetzki (J. Appl. Chem. Russ., 1936, **9**, 353—361).—Trustworthy results are not obtained in the iodometric determination of $O_3$ in air, since $NO_2$, which is invariably produced at the same time as $O_3$, gives the same reactions. $O_3$ is determined by shaking a sample of air (10 litres) with 50 ml. of standard aq. $NaNO_2$ (1 ml. equiv. to 0·0005 mg. of $O_3$) and 2 ml. of 0·01*M*-$MnSO_4$. 3 ml. of Griess-Ilosvay reagent are added to 20 ml. of the solution, which is warmed at 70—80° for 3—5 min., and $H_2O$ is added to 25 ml. The coloration is compared with that given by the standard. R. T.

**Quantitative analysis by the Raman effect of sulphato-nitric mixtures.** J. Chédin (Compt. rend., 1936, **202**, 1067—1069).—The % of $N_2O_5$ in mixtures of $HNO_3$ and $H_2SO_4$ has been determined by observing the Raman spectrum, $N_2O_5$ giving, among other lines, an intense line $\Delta\nu = 1398$ cm.$^{-1}$ The $HNO_3$ is entirely dehydrated up to approx. 15%, and the % of $N_2O_5$ in the mixture is a max. at approx. 20% of $HNO_3$. It follows that in mixtures of oleum and $HNO_3$ the dehydration of $HNO_3$ is complete at a much higher % of $HNO_3$. R. S. B.

**Determination of nitrogen by Kjeldahl's method. Ammonia distillation.** J. Speirs and W. J. Mitchell (J. Inst. Brew., 1936, **42**, 247—250).—Loss of $NH_3$ could not be demonstrated during Kjeldahl distillations carried out by the method of Ford *et al.* (see B., 1933, 842), either in modifications wherein the NaOH was added before or after the commencement of boiling, or with various described modifications of the apparatus (cf. Miller, this vol., 302). Further, the use of air-saturated $H_2O$ or the passage of air through the boiling mixture caused no loss, whilst slow boiling held no advantage. I. A. P.

**Copper selenite as a catalyst in the Kjeldahl nitrogen determination.** E. J. Schwoegler, B. J. Babler, and L. C. Hurd (J. Biol. Chem., 1936, **113**, 749—751).—$CuSeO_3,2H_2O$ is a better catalyst for Kjeldahl digestion than are those at present in use. H. D.

**Kjeldahl decomposition using selenium.** K. Täufel, H. Thaler, and K. Starke (Angew. Chem., 1936, **49**, 265—266).—Se is adequate as a catalyst; addition of $CuSO_4$ gives satisfactory results, but $K_2SO_4$ leads to some loss of N. J. S. A.

**Modified technique for Kjeldahl procedure.** A. Henwood and R. M. Garey (J. Franklin Inst., 1936, **221**, 531—538).—Procedure is outlined for a rapid modification of the macro-Kjeldahl process, using one tenth of the usual quantity of material. J. S. A.

**Determination of nitrate by means of Devarda's alloy.** M. B. Donald (Analyst, 1936, **60**, 249—250).—Reduction is optimal when 1 g. of $NaNO_3$ is treated with 3 g. of alloy and 2 g. of NaOH in 250 c.c. of $H_2O$. E. C. S.

**Drop method of detection of ammonium.** N. A. Tananaev and A. A. Budkevitsch (J. Appl. Chem. Russ., 1936, **9**, 362—363, 369—371).—A drop of conc. aq. NaOH is added to a drop of the solution, which, if turbid, is then filtered through a capillary. A drop of Nessler's reagent is then placed on a drop of the filtrate on filter-paper, when a yellow stain is obtained in presence of $\nless 3\times10^{-7}$ g. of $NH_4^{\cdot}$. If the solution contains Ag, Hg, or Pb, a drop is placed on a drop of 2*N*-NaOH on filter-paper, 2 drops of 2*N*-NaOH are added, and a capillary containing Nessler's reagent is drawn across the spot; a peripheral coloration is obtained in presence of $\nless 2\times10^{-6}$ g. of $NH_4^{\cdot}$. R. T.

**Azorubin, a new reagent for detection of nitrates and nitrites.** F. Skoutil (Chem. Listy, 1936, **30**, 74—77).—1—3 drops of aq. 0·01% azorubin are added to 1—2 c.c. of solution, and 1—2 c.c. of conc. $H_2SO_4$ are added, when a blue ring appears at the $H_2SO_4$–$H_2O$ interface; this will be separated from the aq. layer by a yellow ring if the solution contains $\nless 1{\cdot}25\times10^{-6}$ g. of $NaNO_3$ or $NaNO_2$. The reaction is also given by $ClO_3'$, $BrO_3'$, $IO_3'$, $IO'$, $SeO_3''$, $SeO_4''$, $TeO_4''$, $Fe(CN)_6'''$, $H_2O_2$, $CrO_4'$, $MnO_4'$, and $VO_3'$, but not by $Fe^{\cdots}$, $Fe(CN)_6''''$, or oleum. R. T.

**Effect of fluorine on precipitation of phosphoric acid with ammonium molybdate.** F. W. Neuhaus (Z. anal. Chem., 1936, **104**, 416—417; cf. this vol., 303).—The effect is already well known. J. S. A.

**Colorimetric determination of orthophosphate in presence of meta- and pyro-phosphate.** K. Boratyński (Z. anal. Chem., 1935, **102**, 421—428).—$P_2O_7''''$ and $PO_3'$ do not give the Mo-blue reaction. $PO_4'''$ may be determined colorimetrically in presence of $P_2O_7''''$ and $PO_3'$ by addition of $(NH_4)_2MoO_4$ and reduction with 1 : 2 : 4-$NH_2{\cdot}C_{10}H_5(OH){\cdot}SO_3H$ or *p*-$OH{\cdot}C_6H_4{\cdot}NHMe,H_2SO_4$ at 25°. In presence of a large excess of $P_2O_7''''$ the $(NH_4)_2MoO_4$ must be increased, owing to the formation of a stable pyrophosphate–molybdic compound. J. S. A.

**Colorimetric determination of phosphoric and arsenic acid with ascorbic acid.** R. Ammon and K. Hinsberg (Z. physiol. Chem., 1936, **239**, 207—216).—Ascorbic acid (I) may usefully be used as reducing agent in the method of Lohmann *et al.* (A., 1927, 69). $AsO_4'''$ and (I) can also be determined under certain conditions but determination of $AsO_4'''$ and $PO_4'''$ in presence of each other is possible only with the help of other methods. W. McC.

**Determination of phosphate in presence of arsenate.** J. Courtois (J. Pharm. Chim., 1936, [viii], **13**, 404—418).—$PO_4'''$ is determined by Copaux' approx. method, being pptd. selectively by $Na_2MoO_4$ in presence of $Et_2O$ from $H_2SO_4$ solutions. Alternatively, $AsO_4'''$ may be reduced to $AsO_3'''$ by $SO_2$ in $H_2SO_4$ solution, or in biological fluids by HI. In the latter case $PO_4'''$ is pptd. as $MgNH_4PO_4$, which is redissolved and determined as before. J. S. A.

**Assay of hypophosphites.**—See B., 1936, 475.

**Sources of error in arsenic determination by Gutzeit's reaction on paper strips.** W. Mühlsteph (Z. anal. Chem., 1936, **104**, 333—344).—A crit. review of published methods. Constancy in the humidity of the gas is essential. J. S. A.

**Detection of small amounts of arsenic by electrolytic reduction.** M. T. Koslovsky and A. J. Penner (Mikrochem., 1936, **19**, 89—97).—As, present in 12% aq. $H_2SO_4$ solution, is reduced electrolytically in an undivided cell at a Hg cathode to $AsH_3$. By separating the gases liberated at the anode and cathode, respectively, $10^{-6}$ g. of As may be detected. In alkaline solution $AsO_3'''$, but not $AsO_4'''$, is reduced to $AsH_3$. J. S. A.

**Direct determination of small amounts of arsenic in presence of mercury.** J. Gangl and H. Dieterich (Mikrochem., 1936, **19**, 253—261).—By effecting reduction with Zn in hot solution, As is reduced quantitatively to $AsH_3$ in presence of a large excess of Hg, and is determined titrimetrically from the mirror formed by thermal decomp. of the $AsH_3$ produced. J. S. A.

**Determination of carbon dioxide in carbonates.**—See B., 1936, 406.

**Rapid determinations of carbon dioxide in gaseous atmospheres.**—See B., 1936, 478.

**Sensitive reaction for potassium.** H. Fredholm (Z. anal. Chem., 1936, **104**, 400—405).—Dilituric (5-nitrobarbituric) acid, prepared by direct nitration of barbituric acid at 100°, gives a characteristically cryst. ppt. with K at concns. $>$ 0·09 mg. of K per c.c. The Rb, $NH_4$, Mg, and Ba salts are also sparingly sol. and characteristic in crystal habit. J. S. A.

**Phthalic acid as reagent for optical identification of some metals and alkaloids.** K. P. Yorks and M. L. Willard (Mikrochem., 1936, **19**, 227—229).—Optical properties of K, Co, Cu, Hg, Sr, Zn, Ni, quinine, brucine, and strychnine phthalates are recorded. J. S. A.

**Volumetric determination of sodium.** A. B. Lewin (Z. anal. Chem., 1936, **104**, 406—413).—The conc. neutral or slightly alkaline solution, containing $\ngtr$ 0·1 g. of Na, is treated at $\ngtr$ 12° with saturated aq. $K_2HSbO_4$ (obtained by fusing $Sb_2O_5$ with 6 mol. proportions of $KNO_3$). $Na_2HSbO_4$ is pptd. completely on addition of EtOH. The ppt. is redissolved in $H_2O$, and reduced with $HCl+Na_2SO_3$. $SO_2$ is boiled off, and Sb is finally titrated with 0·02*N*-$KBrO_3$. J. S. A.

**Spectrographic determination of certain elements by the arc process.** K. Konishi and T. Tsuge (J. Agric. Chem. Soc. Japan, 1936, **12**, 216—248).—Minute amounts of elements in soils and plants are determined by examination of their emission spectra. The min. amount of element varies from 1—$5\times10^{-4}$ mg. for Na and Ca to $>$ 0·1 mg. for Cs. The advantages of the method are simplicity, speed, and sensitivity. J. N. A.

**Analysis and separation of the more important anions.** F. Pozna and E. Migray (Annali Chim. Appl., 1936, **26**, 81—83).—The detection of inorg. anions and OAc′ is described. F. O. H.

**Analysis of solutions of salts of heavy metals.** F. Pozna and E. Migray (Annali Chim. Appl., 1936, **26**, 78—80).—A method for the detection of all the common metals in solutions free from Ca, Ba, and Sr is described. F. O. H.

**Simplified method of separating and identifying cations of second group.** E. Chirnoagă (Z. anal. Chem., 1936, **104**, 356—358).—The sulphide ppt. is divided into two portions: (*a*) As is dissolved on boiling with $(NH_4)_2C_2O_4+NH_3$, and may be repptd. with $H_2S$; (*b*) Cd, Bi, Sb, and Sn are dissolved by 2*N*-$HCl+H_2O_2$. Cd is pptd. as CdS from the solution obtained by adding an excess of aq. $NH_3$; Bi, Sb, and Sn as ordinarily. (*c*) The residue ($CuS+HgS$) is dissolved in conc. $HCl+H_2O_2$. J. S. A.

**Microchemical determination of silver.** J. Donau (Mikrochem., 1936, **19**, 108—117).—Ag is determined in the $HNO_3$ solution from the inquartation of Au alloys, or in the $HNO_3$ solution of Ag alloys. Ag is displaced from solution by Cu (in the form of wire) at 100°. Supernatant liquid is sucked off, and the Ag is washed and dried *in situ*. J. S. A.

**Qualitative micro-separations.** A. A. Benedetti-Pichler and W. F. Spikes (Mikrochem., 1936, **19**, 239—244).—Ag, Pb, and Tl, are pptd. with HBr. Pb and Tl are extracted with $H_2O+Br$. Pb is pptd. as $PbSO_4$, which is converted into $K_2PbCu(NO_2)_6$, and $Tl^{III}$ is reduced with $SO_2$ and repptd. as TlI. J. S. A.

**Determination of lead in drinking water.**—See B., 1936, 430.

**Volumetric analysis of lead chromate.**—See B., 1936, 419.

**Detection of thallium.** L. Kuhlberg (Mikrochem., 1936, **19**, 183—186).—$Tl^{III}$ oxidises *o*-$NO_2\cdot C_6H_4\cdot CH(C_6H_4\cdot NEt_2\text{-}p)_2$ (I) (prep. described) to an intense green dye. $Tl^{I}$ is oxidised by $K_3Fe(CN)_6$ to the very insol. $Tl(OH)_3$, which is filtered through a micro-filter. The paper is spotted with (I), dissolved in AcOH; limiting concn. $10^{-7}M$. In presence of other cations, Pb is pptd. with $Na_2SO_4$, and other metals with NaOH before pptg. $Tl(OH)_3$. J. S. A.

**Drop colorimetric determination of copper.** N. A. Tananaev and A. I. Ivanova (J. Appl. Chem. Russ., 1936, **9**, 364—366).—The intensity of coloration obtained when a drop of aq. $K_4Fe(CN)_6$ is placed on a drop of solution is compared with those given by a series of standard Cu solutions. The procedure for determination of Cu in ores is described. R. T.

**Qualitative micro-analysis.** F. Feigl and R. Uzel (Mikrochem., 1936, **19**, 132—143).—(*a*) For the detection of Cu, a drop of the solution under test is treated with 0·1% aq. $K_2TeO_4$ or $KIO_4$ and made alkaline with NaOH. $K_2S_2O_8$ is added, and the solution is heated to 100°. In presence of $\nless$ $0{\cdot}02\times10^{-6}$ g. of Cu a yellow to red coloration is produced, due to the formation of tervalent Cu compounds. $NH_4^{\cdot}$, or an excess of Cr or Mn, should be absent. Conversely, by adding 0·00002*M*-$CuSO_4$, $0{\cdot}5\times10^{-6}$ g. of Te (as $H_6TeO_6$) or $2\times10^{-6}$ g. of $H_5IO_6$ may be detected in presence of other strongly oxidising anions. Te, in presence of 20,000 parts of Se, and $H_5IO_6$ may also be detected by their inhibiting action on the catalytic effect of Cu on the oxidation of $Mn^{\cdot\cdot}$ to $MnO_4'$ by NaOBr. (*b*) $NH_2OH$ is detected by adding $FeSO_4$, and then making alkaline with NaOH. $NH_2OH$ forms $Fe(OH)_3+NH_3$, which is detected by its action on $AgNO_3+MnSO_4$ (A., 1933, 798). (*c*) $Na_2[Fe(CN)_5NO]$ gives with piperidine in AcOH solution the *salt* $Na_3[Fe(CN)_5C_5H_{11}N],6H_2O$, which gives, on filter-paper, a green fleck with $\nless 0{\cdot}05\times10^{-6}$ g. of Co. Hg, Cu, Ag, Pb, Bi, and Ni which interfere are first removed as insol. salts; Fe is converted into $FePO_4$. J. S. A.

**Determination of aluminium by means of aniline.** T. Kozu (J. Chem. Soc. Japan, 1935, **56**, 562—569).—Al can be pptd. from a K alum solution by adding saturated aq. $NH_2Ph$. The $p_H$ of the solution when pptn. is complete is 4·45—4·50. The ppt. is collected, washed, and weighed as $Al_2O_3$. Ch. Abs. (*e*)

**Aluminium alizarinate. Colorimetric determination of aluminium.** A. K. Babko (J. Appl. Chem. Russ., 1936, **9**, 375—378).—The compound $Al(C_{14}H_7O_4)_3$ is formed in presence of considerable excess of alizarin (I), whilst when excess of $Al^{\cdot\cdot\cdot}$ is present a maximally saturated adsorption compound approximating to $Al_2(C_{14}H_7O_4)_3$ is obtained. The rate of increase of the concn. of the lake is < that of $Al^{\cdot\cdot\cdot}$, at const. concn. of (I); at const. concn. of (I) and Al the ratio of (I) to Al in the compound rises with increasing dilution. R. T.

**Detection of gallium using colour reactions.** N. S. Poluektov (Mikrochem., 1936, **19**, 248—252).—Ga gives with alizarin in presence of $NH_3+NH_4Cl$ a bright red lake. The sensitivity is enhanced by concentrating the ppt. at an $Et_2O-H_2O$ interface. Ga, but not Al or In, gives with $K_4Fe(CN)_6+MnCl_2$ in presence of oxidising agents (*e.g.*, $KBrO_3$) a sensitive reddish-brown coloration or ppt. Ga is best separated from other metals by extraction of $GaCl_3$ with $Et_2O$, followed by extraction from the $Et_2O$ layer by means of NaOH. Ga is then pptd. by means of 8-hydroxyquinoline before applying drop tests. J. S. A.

**Determination of manganese in cobalt alloys.**—See B., 1936, 412.

**Colorimetric determination of iron with thiocyanates.** K. Steinhäuser and H. Ginsberg (Z. anal. Chem., 1936, **104**, 385—390).—The red $Fe(CNS)_3$ coloration is stabilised by extracting it with $Et_2O$ saturated with $SO_2$ (I). The solution is acidified with conc. HCl, and treated with KCNS. EtOH is added, and the solution is extracted with (I). The coloured $Et_2O$ solution is photometered by filtered blue or green light. J. S. A.

**Determination of traces of ferric iron in blood serum.**—See this vol., 747.

**Determination of tungsten in wolframite by chlorination.**—See B., 1936, 413.

**Determination of tungsten and silicon in steels by means of perchloric acid.**—See B., 1936, 457.

**Detection and colorimetric determination of tin by means of substituted 1 : 2-dimercaptobenzenes. A specific reagent for tin.** R. E. D. Clark (Analyst, 1936, **60**, 242—245).—A few drops of 0·2% 4 : 1 : 2-$C_6H_3Cl(SH)_2$ or 4 : 1 : 2-$C_6H_3Me(SH)_2$ in aq. NaOH are added to the solution of Sn in $\ngtr$ 15% aq. HCl; on warming in presence of $\nless$ 1 p.p.m. of $Sn^{II}$, a pink or red colour is formed within a few sec. With $Sn^{IV}$ the colour takes longer to develop and the test is less sensitive. Bi gives a brick-red ppt. which cannot be mistaken for the magenta-red of Sn. The reaction is applied to the colorimetric determination of Sn, by means of which 1·5—6 p.p.m. may be determined to within 10%. E. C. S.

**Drop method of detection of antimony.** N. A. Tananaev and L. M. Rabinovitsch (J. Appl. Chem. Russ., 1936, **9**, 369—371).—The solution is heated with HCl and Fe for 3—4 min., allowed to settle, the supernatant liquid is poured off, and the sediment (Pb, Hg, Bi, Cu, Sb, and excess of Fe) is washed by decantation and transferred as a suspension to a second tube. It is then treated with hot conc. $HNO_3$, when a white ppt. is obtained in presence of $\nless$ 0·1 mg. of Sb. R. T.

**Analytical chemistry of tantalum, niobium, and their mineral associates. XXX. Beryllium.** W. R. Schoeller and H. W. Webb (Analyst, 1936, **60**, 235—242; cf. A., 1935, 838, 1217).—For its determination, the ppt. of BeO obtained by treatment with aq. $NH_3$ or tannin (I) in presence of alkali sulphate is fused with $Na_2CO_3$ and extracted with $H_2O$, as for the separation of Be from Al (cf. A., 1912, ii, 687); BeO is quantitatively pptd. from aq. $NH_3$-tartrate by (I). The earth-acid ppt. obtained by tartaric hydrolysis (cf. A., 1930, 184) does not occlude BeO. Ti, Nb, and Ta are separated from Be as well as from Zr etc. by pptn. with (I) from $C_2O_4''$ solution half-saturated with $NH_4Cl$ (cf. A., 1932, 1012). U is separated from Be by pptn. as ferrocyanide. E. C. S.

**Detection and determination of gold by means of filter-paper impregnated with reducing substances.** R. N. Costeanu (Z. anal. Chem., 1936, **104**, 351—355).—The alloy is treated with $HNO_3$ to remove Ag and Cu, and the residue is dissolved in $HCl+HNO_3$, and diluted to a known vol. A standard drop of the solution is applied to paper impregnated with $SnCl_2$, benzidine, quinol, $NH_2OH,HCl$, or other suitable reducing agent, and the intensity of the fleck obtained is matched against that given by solutions of known [Au]. J. S. A.

**Liquid-operated thermostat.** A. R. Pearson and R. E. Norris (J.S.C.I., 1936, **55**, 127—128T).—Part of the wall of the regulator vessel is made in re-entrant form, of material having high thermal conductivity and expansion.

**Apparatus for heating inflammable solvents.** B. Melkon (Amer. J. Pharm., 1936, **108**, 95—98).—An asbestos-lined paint can enclosing an electric lamp is used as heating bath. R. S. C.

**Measurement of the thermal conductivity of gases.** T. H. Laby (Nature, 1936, **137**, 741).—Advantages of the use of a thick in preference to a thin wire are discussed. L. S. T.

**Fluorescence thermoscope.** H. Eichler (Chem.-Ztg., 1936, **60**, 357).—Solutions of Magdala-red in solvents containing OH- or $CO_2H$-groups change from violet to yellowish-red with sudden appearance of fluorescence when the m.p. of the solvent is exceeded. This property is utilised in a thermoscope, comprising a thin-walled glass tube containing such a solution, loaded with Pb at one end so as to float in liquids, which permits ready observation when a certain temp. is exceeded. Solvents suitable for the specified temp. are: *o*-$C_6H_4(CO_2H)_2$ (213°), *o*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ (159°), BzOH (121°), *m*-$C_6H_4(OH)_2$ (118°), thymol (51°), PhOH (42°), *p*-cresol (36°), *o*-cresol (31°), AcOH (17°), $HCO_2H$ (9°), and *m*-cresol (3°). For intermediate temp. mixed solvents are used, whilst below 0° the solvent can be $CH_2O$, MeOH, EtOH, glycerol, or $COMe_2$. J. W. S.

**Spectropolarimetry with metallic mirrors in the far ultra-violet.** R. Servant (Compt. rend., 1936, **202**, 476—477).—An arrangement suitable for polarimetry with light sources between λ 2500 and 1850 A. is described. F. L. U.

**Technique for obtaining *X*-ray powder patterns.** R. A. Stephen and R. J. Barnes (Nature, 1936, **137**, 532—533; cf. this vol., 45). L. S. T.

**Demonstrating and measuring approximately the index of refraction of crystalline substances for *X*-rays.** H. C. Hoyt and G. A. Lindsay (Physical Rev., 1936, [ii], **49**, 498—501).—By reflecting the same spectral line simultaneously from two faces of a crystal by turning the crystal so that for the proper reflecting angle the rays fall at the intersection of the two faces, *n* can be obtained by a simple calculation from the width included between the reflected and refracted portions of the line. The method has been confirmed for a cerussite crystal. N. M. B.

**Drop-plate for the observation of turbidity in the dark field.** S. Wehrli (Helv. Chim. Acta, 1936, **19**, 505—506).—A method of illuminating small drops of liquid in the investigation of pptn. reactions is described. M. S. B.

**Measurement of dielectric constant for very short waves with a registering apparatus.** R. Freymann (Compt. rend., 1936, **202**, 952—954).—Drude's method is applied, the resonance curve being recorded photographically with a galvanometer. Measurements are recorded for certain aromatic N compounds (λλ 3·72—2·41 m.). H. J. E.

**Counter for α-particles.** S. S. Vassiliev (Nature, 1936, **137**, 533). L. S. T.

**Characterisation and designation of new counters for elementary rays and photo-electrons. Spark counter.** H. Greinacher (Helv. phys. Acta, 1935, **8**, 265—266; Chem. Zentr., 1935, ii, 1219).—Counters based on a spark discharge between metal and liquid, or dissimilar metal electrodes, are described. J. S. A.

**New counting methods for elementary rays and photo-electrons.** H. Greinacher (Z. tech. Physik., 1935, **16**, 165—170; Chem. Zentr., 1935, ii, 1219; cf. preceding abstract). J. S. A.

**Comparison of photo-emissive and photo-voltaic devices [for measuring radiant energy].** E. D. Wilson (Trans. Electrochem. Soc., 1936, **69**, Preprint 19, 221—228).—Useful characteristics of each type of photo-cell are discussed. By suitable construction and the use of various filters, photo-electric devices can be suited to any particular range of the spectrum, from the ultra-violet to the near infra-red (λ 1·4 μ). By using fluorescent screens and suitable filters the intensity of *X*-ray radiations can be measured. J. W. C.

**Barrier layers and photoelectricity.** J. Roulleau (Compt. rend., 1936, **202**, 470—472; cf. A., 1935, 585).—In cells of the metal–$Cu_2O$ type the photo-electric effect and contact rectification are both independent of the sp. resistance of the $Cu_2O$ in bulk, whilst both increase with the contact resistance and are therefore related to it. F. L. U.

**Electrophoresis cell for microscopic observations.** M. E. Smith and M. W. Lisse (J. Physical Chem., 1936, **40**, 399—412).—A cell of new design is described. Observations are made at the axis, where the electro-osmotic flow is zero, and the velocity gradient a min. Mobilities of quartz particles in $H_2O$ so measured agree with vals. determined by the usual methods. The respective electrophoretic and electro-osmotic velocities of quartz in $H_2O$ and of $H_2O$ in a quartz tube are 3·0 and −3·1 μ per sec. per volt per cm. F. L. U.

**$p_H$ conversion chart.** W. H. Goss (J. Washington Acad. Sci., 1936, **26**, 150—156).—The chart facilitates conversion of e.m.f. into $p_H$ vals. with reference to various electrodes. A. G. P.

**Automatic precision burettes.** F. Köoler (Chem. Fabr., 1936, **9**, 115—116).—The two types of burette described are filled automatically from the supply bottle to which they are attached, by the use of compressed air or suction, respectively. A. B. M.

**Precision apparatus for mixing gases in various proportions.** B. N. Singh and P. B. Mathur (Science, 1936, **83**, 309—310). L. S. T.

**Washing tube for gas analyses.** O. Hackl (Z. anal. Chem., 1936, **104**, 359).—Priority is claimed over Cauer (this vol., 577). J. S. A.

**Drainage errors and U-tube viscosimeters.**—See B., 1936, 436.

**Suspended-level viscosimeter.**—See B., 1936, 436.

**Specific gravity balance.** P. F. Kerr (Amer. Min., 1936, **21**, 121—124).—The apparatus described is particularly suitable for crystals, small masses of minerals, or gem stones. L. S. T.

**Arsenic combustion tubes.** G. Lockemann (Angew. Chem., 1936, **49**, 252).—Tubes with 2 and 3 compartments separated by constrictions, for use in the Marsh–Liebig method of As detection, are described. M. S. B.

**Sucrose as a standard for obtaining absolute viscosities.** T. H. Messenger (J. Res. Assoc. Brit. Rubber Manufrs., 1936, **5**, 25—35).—Viscosities and *d* of aq. sucrose solutions are tabulated and the use of such solutions as standards in viscosimetry is demonstrated. R. S.

**Micro-Kjeldahl flask.** A. Soltys (Mikrochem., 1936, 19, 304—305).—By setting the neck at an angle, loss by bumping or splashing is avoided. J. S. A.

**Simplified form of Schöbel heating mortar.** Schott und Gen. (Mikrochem., 1936, 19, 164; cf. A., 1934, 425). J. S. A.

**Apparatus for recrystallisation of small amounts.** B. K. Blount (Mikrochem., 1936, 19, 162—163).—The substance, in a sintered glass funnel, is suspended below the condenser from which the solvent is refluxed. J. S. A.

**Demountable centrifuge tubes for gravimetric determinations.** S. D. Elek (Mikrochem., 1936, 19, 129—131). J. S. A.

**Shaker with lengthwise and cross motions.** G. Lockemann and P. Loch (Chem. Fabr., 1935, 9, 200). D. R. H.

**Mirrors obtained by evaporation in a vacuum.** L. Dunoyer (Compt. rend., 1936, 202, 474—476).—In depositing a metallic mirror (*e.g.*, Al) by evaporation it is essential for good adherence that the residual gas pressure should correspond with a mean free path of the same order as the max. distance of the vapour source from the surface to be covered. Deposits of uniform thickness can be obtained by suitable relative movement of source and surface. Flaws in the receiving surface, or defects in polishing, are reproduced in the deposited metal. In the absence of any defects the metallic surface, unlike chemical deposits, shows no diffuse reflexion. F. L. U.

**Comparative method for measuring aqueous vapour and dissociation pressures, with some applications.** E. M. Collins and A. W. C. Menzies (J. Physical Chem., 1936, 40, 379—397; cf. A., 1934, 248).—The method described depends on measurement (by weighing) of the change in concn. of a small amount of aq. $H_2SO_4$ during the attainment of equilibrium, through the vapour phase, with a large amount of the material, the aq. v.p. of which is required. The substances are placed in an exhausted sealed tube, and equilibrium is approached from both directions. The method is suitable for temp. up to 130°. Data for six salt hydrate systems are recorded. F. L. U.

**Rapid and exact transference of a precipitate to a filter.** G. G. Longinescu and I. I. Prundeanu (Bull. Acad. Sci. Roumaine, 1936, 17, 151—154).—Pptn. and washing are carried out in a funnel, and the ppt. is transferred directly to the crucible. H. G. R.

**Sliding ground-glass joint.** J. Fine (Rev. Sci. Instr., 1936, [ii], 7, 192).—A short connecting piece has joints at each end ground on the inside, both tapers pointing in the same direction. It can therefore be telescoped over the tube which enters it at its narrower end. C. W. G.

**Simplified apparatus for high hydrostatic pressures.** L. H. Adams (Rev. Sci. Instr., 1936, [ii], 7, 174—177).—A simple piston is forced into a 19-mm. hole in a steel block. Leakage is prevented by a rubber plug and a layer of oil moving ahead of the piston. Pressure is measured by a Hg-in-glass piezometer tube inside the piston. 10,000 atm. can be reached. C. W. G.

**Average pore size of diaphragms.** H. B. Bull and L. S. Moyer (Science, 1936, 83, 242—243).—The radius of powdered quartz diaphragms ranged from 1·4 to 30 μ according to the degree of grinding, whilst that of cellulose membranes varied from 0·88 to 0·98 μ. L. S. T.

**Cullen chemical manuscript of 1753.** L. Dobbin (Ann. Sci., 1936, 1, 138—156).

**Thomas Cochrane's MS. notes of Black's chemical lectures, 1767—1768.** D. McKie (Ann. Sci., 1936, 1, 101—110).

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## Geochemistry.

**Explanation of the relatively large concentration of $O^{18}$ in the atmosphere.** C. H. Greene and R. J. Voskuyl (J. Amer. Chem. Soc., 1936, 58, 693—694).—Attention is directed to the rôle played by the respiration of plants. E. S. H.

**Carbon dioxide content of atmospheric air.** J. B. S. Haldane (Nature, 1936, 137, 575).—An improved form of the Haldane gas analysis apparatus adapted for the determination of $CO_2$ only permits rapid analyses with an accuracy of 1 or 2 parts in $10^5$ using 20 c.c. of air. The $CO_2$ in country air at 4 to 70 ft. above ground level varied between 21 and 44 parts in $10^5$. Diurnal variation due to photosynthesis is marked between July and October, but not in December. Exhalation of $CO_2$ from the soil is definite, the mean excess being 5·4 parts in $10^5$ at ground-level compared with a height of 4 ft. above. The effect of combustion is marked, the average val. for London being 65 parts in $10^5$. Other variations due to causes at present uncertain are recorded. L. S. T.

**Alkali metals in natural waters.** R. Bossuet (Compt. rend., 1936, 202, 1162—1164).—A large no. of samples of natural $H_2O$ have been examined in the $O_2$–$C_2H_2$ flame for alkali metals. The presence of Na and K increases the sensitivity of the test for Rb and Cs. All five alkali metals have been found in most cases, but Cs is absent (*i.e.*, $< 10^{-3}$ mg. per litre) in certain cases where $Ca(HCO_3)_2$ or $CaSO_4$ predominate, and in some other samples. M. S. B.

**Chemical and physico-chemical analysis of the mineral water of Fontecchio.** L. Bellucci, M. Sgarzi, and A. Barillaro (Annali Chim. Appl. 1936, 26, 130—138).—The $H_2O$ has an odour of $H_2S$. Analytical data, physico-chemical properties, and radioactivity are recorded. L. A. O'N.

**Activity of non-pathogenic bacteria in the thermal water of Aix-les-Bains and Aix-Burtscheid. II.** A. Schloemer (Z. Unters. Lebensm., 1936, 71, 268—273; cf. A., 1933, 691; 1934, 53).—The $NO_2'$ in the thermal $H_2O$ is due entirely to the growth of nitrifying bacteria. The deposit is largely due to the action of $CaCO_3$- and $SiO_2$-bacteria, but deposition of $CaCO_3$ is facilitated by the low $CO_2$ content of the $H_2O$. E. C. S.

**Chemical and biological characteristics of the Lake of Massaciuccoli.** G. Brunelli and G. Cannicci (Atti R. Accad. Lincei, 1935, [vi], **22**, 598—604).—A preliminary description. O. J. W.

**Carbon dioxide and hydrogen ion content of the lake waters of N.E. Wisconsin.** C. Juday, E. A. Birge and V. W. Meloche (Trans. Wis. Acad. Sci., 1936, **29**, 1—82).—Data for 518 lakes are recorded, showing annual variation and variation with depth. C. W. G.

**Analysis of thermal spring at Lipik.** S. Miholić (Bull. Soc. Chim. Yougoslav., 1935, **6**, 169—177).—The I content has diminished exponentially since 1870. R. T.

**Mineral water of Rogaska Slatina.** A. Režek (Bull. Soc. Chim. Yougoslav., 1935, **6**, 179—187).—The $H_2O$ activates salivary and pancreatic amylases (optimum $p_H$ 6·0—6·4 and 6·0—6·8, respectively). The mechanism of activation is discussed. R. T.

**Boron content of oil-field waters.** S. G. Zeitlin (Compt. rend. Acad. Sci. U.R.S.S., 1936, **1**, 123—126).—Data are recorded for samples from the Baku, Dagestanskije Ogni, Novogroznenskoie, and Turkestan regions. The borax content of the dry residue was 0·5—0·6%. H. J. E.

**Waters, magmatic and meteoric.** F. E. Keep (Econ. Geol., 1936, **31**, 118—121).—A discussion (cf. A., 1935, 1343) relating mainly to Witwatersrand water. L. S. T.

**Concentration of $D_2O$ in natural ice. III.** E. Baroni and A. Fink (Monatsh., 1936, **67**, 193—195; cf. A., 1935, 953).—Snow, independent of age, has the same $D_2O$ content as normal $H_2O$, but hoar frost samples have 15—50% greater concn. than normal. It is concluded that concn. of $D_2O$ is possible under natural conditions such as hoar frost formation and slow evaporation of glaciers. J. W. S.

**Theoretical consideration of ideal liquid inclusions.** S. T. Yuster (Amer. J. Sci., 1936, [v], **31**, 363—372).—Calculations are made of the temp. and pressures which existed at the time when liquids and gases were enclosed in crystals. L. J. S.

**Crystallisation process of basalt.** T. F. W. Barth (Amer. J. Sci., 1936, [v], **31**, 321—351; cf. A., 1931, 708, 816; 1932, 494).—Further discussion on the crystallisation of felspar and pyroxene in basaltic magma with progressive alteration in the composition of the magma. L. J. S.

**Occurrence of claudetite in Imperial County, California.** V. C. Kelley (Amer. Min., 1936, **21**, 137—138).—An occurrence in a vein composed mainly of kaolin, gypsum, halloysite, and S is described. L. S. T.

**Accessory minerals of the Wolf Mountain granite, Llano County, Texas.** R. E. McAdams (Amer. Min., 1936, **21**, 128—135).—The percentages of the accessory minerals biotite, hornblende, magnetite (I), muscovite, apatite (II), zircon (III), titanite (IV), monazite, rutile, chlorite, fluorite (V), garnet, tourmaline, brookite, ilmenite, and pyrite are tabulated. A yellow, isotropic mineral, as yet unidentified, is also present. The Wolf Mountain granite, the Bear Mountain granite, and the quartz porphyry have different accessory mineral assemblages. The former and the Lone Grove granites apparently had a common parent magma. The Bear Mountain granite, with its more abundant (V), is probably younger than these granites, and of the same age as the quartz porphyry. The ratio of (III) to (II) appears to increase toward the bottom of the Wolf Mountain mass, where (I) is also conc. The % of (IV) increases as the border of Wolf Mountain is approached. L. S. T.

**Chemical composition of the eruptive rock of Cupaello (Rieti).** F. Rodolico (Atti R. Accad. Lincei, 1935, [vi], **22**, 469—472).—The following composition is given: $SiO_2$ 42·64, $TiO_2$ 0·87, $P_2O_5$ 1·26, $SO_3$ 0·62, $Al_2O_3$ 7·01, $Fe_2O_3$ 5·78, FeO 1·66, MnO 0·16, MgO 10·86, CaO 14·53, $Na_2O$ 0·71, $K_2O$ 5·61, $H_2O+$ 6·22, $H_2O-$ 2·28, total 100·21%; *d* 2·61. O. J. W.

**New crystal-bearing glass from Macusani (Peru).** F. Heide (Naturwiss., 1936, **24**, 281—282).—A description of a glass containing crystals, and identical with that discovered by Linck (Chem. Erde, 1926, **2**, 157) at Paucartambo (Peru), is given. A. J. M.

**Ore-bearing zones of the metal deposits of Karakstan.** N. Kassin (Problem. Sovet. Geol., 1933, **4**, 58—63).—The deposits are described. Ch. Abs. (*e*)

**Radium discoveries in N.W. Canada.** H. S. Spence (Sands, Clays and Min., 1935, **2**, No. 3, 8—23).—A review. H. J. E.

**Zermattite and schweizerite from Dshemarakly-tjube Mt. in the Karatschai region, Caucasus.** D. Serdiutschenko (Mém. Soc. russe Min., 1932, **61**, 94—100).—These minerals were deposited from $H_2O$ solutions genetically connected with the intrusion of a quartz-keratophyre, and are exceptionally rich in CaO and $Al_2O_3$. Ch. Abs. (*e*)

**Petrology of the Hartley district. III. Contact metamorphism of the upper Devonian (Lambian) series.** G. A. Joplin (Proc. Linnean Soc. N.S. Wales, 1935, **60**, 16—50). Ch. Abs. (*e*)

**Bolivian tin belt.** F. Ahlfeld (Econ. Geol., 1936, **31**, 48—72).—The Bolivian metallogenetic province contains chiefly Sn, W, Mo, As, Bi, Cu, Zn, Pb, Sb, commonly Ag, and rarely Au, Ni, Co, and Hg. B is very common, whilst Be and U are absent. The minerals and their paragenesis, the rock alteration, and the ore deposits are described, and the genesis of the deposits is discussed. L. S. T.

**Hydrothermal oxidation of manganese minerals.** S. A. Trengove (Econ. Geol., 1936, **31**, 29—47).—Rhodochrosite (I) is readily decomposed and oxidised by steam in 24 hr. at temp. $> 170°$. Pyrolusite is probably present in the alteration product. Oxidation increases with temp. up to approx. 300°, above which temp. complex alteration products are formed. High pressure or the addition of $CO_2$ to the steam retards decomp. Oxidation occurs slowly at high pressures when small amounts of HCl are present and more rapidly at pressures nearer 1 atm. (I) is stable at room temp. in air, and at 250° when steam or other sources of $O_2$ is absent. Decomp. commences at approx. 275° and oxidation due to the decomp. of the contained $CO_2$ occurs. Fowlerite shows no hydrothermal oxidation at temp. $\not>$ 400°. The bearing of these results on the genesis of Mn oxide ore deposits in various parts of the world is discussed. L. S. T.

**Battle Branch gold mine, Auraria, Georgia.** C. F. Park, jun., and R. A. Wilson (Econ. Geol., 1936, **31**, 73—92).—The mineralogy of the deposit is unusual and three stages are recognised. An early high-temp. stage produced coarsely cryst. silicates, such as garnet (almandite common), cummingtonite, kyanite, and micas, probably formed by recrystallisation of minerals in the country rock. During an intermediate stage ankerite, quartz, and pyrrhotite were deposited, and the last stage produced chlorite, galena (I), and Au. The Au in the rich shoots is contemporaneous with (I) and is of hypogene origin. The soil and saprolite extend to a max. depth of 80 ft., and mechanical enrichment of Au has occurred in the latter. L. S. T.

**Geology and ore deposits of the Central Patricia gold mine, Ontario.** J. M. Cormie (Econ. Geol., 1936, **31**, 93—103).—These ore bodies are sulphide-rich masses formed by fracture filling and by replacement of the Fe formation in which they occur. Pyrrhotite (I) and arsenopyrite (II) are predominant, whilst chalcopyrite (III) and pyrite (IV) are less abundant. The non-metallic minerals are quartz (black and white), chlorite, and carbonate. Au is the only economically valuable mineral in the ores and is associated with all the sulphides except (IV); Ag is present in minor amounts. The mineral succession is (IV), quartz veins; fracturing; (I), (III), and gangue; fracturing; (II); fracturing. The hypothermal genesis of the deposit is discussed. L. S. T.

**Cinnabar deposits in S.W. Arkansas.** N. H. Stearn (Econ. Geol., 1936, **31**, 1—28).—The deposits occurring in the Athens Plateau are described. The ores are mainly fracture fillings in the sandstone with dickite, cinnabar, and quartz as the principal minerals, and small amounts of pyrite, stibnite, and siderite. They are hydrothermal in origin. The tenor of the ore in place is approx. 10 lb. of Hg per ton of rock. Secondary minerals are metacinnabar, Hg, eglestonite, livingstonite, calomel, chalcedony or opal, hydrated Fe oxide, and stibiconite. L. S. T.

**High-temperature mineral associations at moderate to shallow depth.** B. S. Butler (Econ. Geol., 1936, **31**, 115—118).—A discussion (cf. A., 1935, 955). L. S. T.

**Gabbros and associated xenolithic complexes of the Haddo House district, Aberdeenshire.** H. H. Read (Quart. J. Geol. Soc., 1935, **91**, 591—638).—The country rocks into which the Haddo House igneous masses intrude consist of andalusite-cordierite-schists, pebbly grits, and cordierite-biotite-gneisses. The gabbro mass consists of olivine- and quartz-gabbro, both considered to be of primary igneous origin, and norite and cordierite-norite which contain abundant xenoliths. The mechanism of the production of the noritic rocks, by assimilation of argillaceous material, is discussed. The gabbros and their xenolithic complexes are intruded by a later granite and by innumerable granitic and pegmatitic dykes. The conditions of formation of monomineralic calc-silicate rocks, such as those of diopside and wollastonite, are discussed. L. S. T.

**Base of the Gault in Sussex.** J. F. Kirkaldy (Quart. J. Geol. Soc., 1935, **91**, 519—537).—The glauconitic sandy clays and layers of hard phosphatic nodules composing the base of the Gault and a bed of limonitic grit are described. Conditions of deposition of the beds are discussed. L. S. T.

**Basic intrusive rocks associated with the Cambrian inlier near Malvern.** F. G. H. Blyth (Quart. J. Geol. Soc., 1935, **91**, 463—478).—A petrological and chemical examination of minor intrusions in the Cambrian strata near Eastnor, Herefordshire. L. S. T.

**Age relations of the Ward ores, Boulder County, Colorado.** E. E. Wahlstrom (Econ. Geol., 1936, **31**, 104—114).—Structure, paragenesis, and age relations of the ore deposits of the Ward district are discussed. The predominant mineralisation is auriferous quartz–pyrite–chalcopyrite ores occasionally with small amounts of molybdenite, wolframite, sphalerite, and specularite. At White Raven mine important amounts of galena–Ag carbonate ore occur. The Au–Cu ore was probably deposited under conditions of medium to high temp. and high pressure from solutions originating from the same magma chamber which gave rise to the Tertiary (?) intrusives. The Pb–Ag ore was probably deposited under conditions of low to medium temp. L. S. T.

**Occurrence and properties of herzenbergite.** P. Ramdohr (Z. Krist., 1935, **92**, 186—189).—A description of naturally occurring SnS. B. W. R.

**Dielectric constant of mineral powders.** J. L. Rosenholtz and D. T. Smith (Amer. Min., 1936, **21**, No. 2, 11 pp.).—Data for 160 minerals are recorded. C. W. G.

**Scheelite from the mines of Gerrei in Sardinia.** A. Pelloux (Atti R. Accad. Lincei, 1935, [vi], **22**, 554—556).—Crystallographic data are recorded. O. J. W.

**Geochemical frequency of barium.** C. J. van Nieuwenburg and R. H. Dewald (Rec. trav. chim., 1936, **55**, 263—266).—The Ba content of igneous rocks is $<$ the Sr content. E. S. H.

**Enrichment of heavy spar by alkaline weathering solutions in a Frankish keuper-arkose, and its regional and geochemical significance.** S. Klein (Z. deut. geol. Ges., 1935, **87**, 320—332; Chem. Zentr., 1935, ii, 1152).—The origin of $BaSO_4$ deposits by the solvent action of alkali carbonates on felspar is discussed. J. S. A.

**Granitic injection processes in the Columbia quadrangle, South Carolina.** T. L. Kesler (J. Geol., 1936, 44, 32—44).—The effects of intrusion of granite are described. L. S. T.

**Clay colloids as a cause of bedding in sedimentary rocks.** W. D. Keller (J. Geol., 1936, 44, 52—59).—Colloidal clay of the montmorillonite-beidellite group extracted from the Putnam soil of Missouri flocculates to relatively coarse aggregates oriented so as to resemble crystals. Their platy shape resembles that of the mineral in a bedded clay shale. The possibility that the lamination of shale develops from deposition of colloidal clay is discussed. L. S. T.

**Probable non-existence of arsenoferrite.** M. J. Buerger (Amer. Min., 1936, 21, 70—71).—*X*-Ray examination of the apparently isotropic mineral of composition corresponding with $FeAs_2$ described by Foshag and Short (A., 1931, 817) shows that the mineral is not cubic and that it is identical with lollingite. L. S. T.

**X-Ray powder diffraction data for antlerite and brochantite.** A. W. Waldo (Amer. Min., 1936, 21, 71—73).—The data previously given for antlerite (I) (A., 1935, 1474) apply to brochantite and not to (I). L. S. T.

**Andalusite in pegmatite.** J. Murdoch (Amer. Min., 1936, 21, 68—69).—Pegmatite dykes cutting the magnesite deposits at Winchester, California, contain reddish-brown andalusite (I). Sillimanite replaces some of the (I). L. S. T.

**Bustamite from [Saline Valley,] Inyo County, California.** J. Murdoch and R. W. Webb (Amer. Min., 1936, 21, 69—70).—Bustamite occurs in numerous boulders of a silicate rock. L. S. T.

**Analyses of thulite.** S. A. Northrop (Amer. Min., 1936, 21, 73).—An additional analysis is recorded (this vol., 308). L. S. T.

**Distribution of the chief mineral deposits of Morocco.** F. Blondel and J. Bondon (Compt. rend., 1936, 202, 1197—1198).—Recent data on the age, distribution, and origin of the different mineral deposits of Morocco are summarised. M. S. B.

**Ligneous substances in lacustrine materials.** J. F. Steiner and V. W. Meloche (Trans. Wis. Acad. Sci., 1935, 29, 389—402).—Analyses for C, N, protein, and lignin are given. C. W. G.

**Vanadium in the petroleums and bitumens of the U.S.S.R.** A. P. Vinogradov and G. G. Bergman (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 349—352; cf. A., 1934, 1380).—The distribution of V in the petroleums and bitumens of the U.S.S.R. has been determined. Deposits of the Devonian period contain the highest and those of the Jurassic period the lowest % of V. From much of the data it appears that V occurs ∝ the % of org. matter in the rock, in Ishma asphaltite. The view that V passes into the petroleum from aq. solution in presence of $H_2S$, the V being held as $V_2S_5$, is considered disproved. It is probable that the V comes from the mud of continental sea basins in which V has been conc. by marine organisms. R. S. B.

**Extra-terrestrial hydrocarbons and petroleum genesis.** F. M. Van Tuyl and B. H. Parker (Bull. Amer. Assoc. Petroleum Geol., 1935, 19, 900—902).—A discussion. Ch. Abs. (*e*)

**Age and conditions of formation of brown coals in the Upper Zeya plain.** G. E. Brikov (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 355—359).—Brown coals of *d* 1·44 found in the Soktakhan mountains are described. R. S. B.

## Organic Chemistry.

**Structural chemistry.** N. V. Sidgwick (J.C.S., 1936, 533—538).—Presidential address.

**Action of aluminium chloride on paraffins. Autodestructive alkylation.** V. N. Ipatiev and A. V. Grosse (Ind. Eng. Chem., 1936, 28, 461—464).—*n*-$C_4H_{10}$, -$C_6H_{14}$, -$C_7H_{16}$, or ββδ-trimethylpentane with $AlCl_3$ and HCl gives complex mixtures of paraffins of lower and higher mol. wt. together with unsaturated hydrocarbons according to four types of reaction: (*a*) formation of paraffin and olefine of lower mol. wt.: (*b*) addition of olefine to paraffin; (*c*) isomerisation regarded as (*a*) followed by (*b*); (*d*) polymerisation of olefines followed by (*b*). The products were separated by Podbielniak distillation, b.p. and $n_D^{20}$ being recorded for the fractions obtained. F. R. G.

**Isomerisation of hydrocarbons. II. Isomerisation of *n*-hexane and *n*-octane in presence of aluminium chloride.** B. L. Moldavski, M. V. Kobilskaja, and S. E. Lifschitz (J. Gen. Chem. Russ., 1935, 5, 1791—1797).—Up to 30% of *n*-$C_6N_{14}$ or -$C_8H_{18}$ is converted into *iso*-$C_6H_{14}$ or -$C_8H_{18}$ by the action of $AlCl_3$ at 20—90°. The velocity of the reaction is greatly increased by HCl. R. T.

**Preparation of *iso*octane.** G. S. Parks and S. S. Todd (Ind. Eng. Chem., 1936, 28, 418—419).—The temp. conditions for the conversion of *iso*butene into ββδ-trimethylpentane are deduced from thermochemical data. F. R. G.

**Methylnonanes.** G. Calingaert and H. Soroos (J. Amer. Chem. Soc., 1936, 58, 635—636).—The following are obtained by simultaneous dehydration and hydrogenation of the alcohols quoted with $H_2$ (200 atm.) and Raney Ni at 250° (after the preliminary absorption of $H_2$ ceases, the $H_2O$ formed is removed and the product reduced further): β-methylnonane (I), b.p. 166·8°/760 mm., m.p. $-74·69\pm0·05°$ (β-methylnonan-γ-ol, from $MgPr^{\beta}Br$ and *n*-$C_6H_{13}$·CHO); γ-methylnonane (II), b.p. 167·8°/760 mm., m.p. $-84·86\pm0·03°$ (γ-methylnonan-γ-ol, from MgEtBr and Me *n*-hexyl ketone); δ-methylnonane, b.p. 165·7°/760 mm., m.p. $-101·62\pm0·05°$ (f.-p. and m.-p. curves indicate a second form of m.p. $-99\pm0·1°$) (δ-methylnonan-δ-ol, from $MgPr^{a}Br$ and Me *n*-amyl ketone); ε-methylnonane, b.p. 165·1°/760 mm., m.p. $-86·8\pm0·03°$ (ε-methylnonan-ε-ol, from $MgBu^{\alpha}Br$ and EtOAc). Vals. of $d_4^{20}$, $n_D^{20}$, and crit. solution temp. in $NH_2Ph$ are given. The influence of structure on the physical properties is discussed. The data for (I) and (II), compared with *n*-decane, are in agreement with those predicted (this vol., 309). H. B.

**Olefine elimination.** E. D. Hughes and C. K. Ingold (Chem. and Ind., 1936, 312—313, 422).—Polemical with Taylor (this vol., 587).

**Olefine formation.** W. Taylor (Chem. and Ind., 1936, 383—384).—Polemical (see above).

**Polymerisation. XV. Polymerisation of ψ-butylene.** S. V. Lebedev and S. M. Orlov. **XVI. Polymerisation of *iso*butylene by the action of floridin at low temperatures.** S. V. Lebedev and J. A. Borgman (J. Gen. Chem. Russ., 1935, **5**, 1589—1594, 1595—1606).—XV. $CHMe{:}CHMe$ (I) yields 80—85% of polymerides when left with floridin at room temp. for 6 months; the product contains 43% of the dimeride (II), b.p. 115—116°/756 mm., and 15—18% of the trimeride (III) of (I), b.p. 78—79°/18 mm. (II) is oxidised by $KMnO_4$ in aq. $COMe_2$ at room temp. to yield $COMe{\cdot}CHMeEt$ (IV), *γδ-dimethylhexane-βγ-diol* (V), b.p. 110—112°/14 mm., m.p. 55°, *Me α-hydroxy-αβ-dimethylbutyl ketone* (VI), b.p. 116—118°/14 mm. (*semicarbazone*, m.p. 170°), COMeEt, AcOH, and $EtCO_2H$; it is hence concluded that (II) is $CHMeEt{\cdot}CMe{:}CHMe$. The oxidation of (II) proceeds as follows: (II) → (V) → (VI) → (IV) → $COMeEt+EtCO_2H+AcOH$.

XVI. The % polymerisation of $CMe_2{:}CH_2$ in presence of floridin increases to a max. as the temp. falls to −65°, and is greatest when the activation temp. of the catalyst is 300°. The mol. wt. of the polymerides rises uninterruptedly with falling temp.; formation of products of high mol. wt. is most actively catalysed by floridin activated at 200°. The mol. wt. of the polymerides varies from 112 to 12,000. The polymerides obtained at −70° with floridin activated at 300° consist of $C_8N_{16}$ 3·4, $C_{12}H_{24}$ 20·7, $C_{16}H_{32}$ 15·3, $C_{24}H_{48}$ 10·8, $C_{28}H_{56}$ 5·4, and higher polymerides 44·4%. R. T.

**Action of certain silicates on hydrocarbons possessing the *tert.*-butyl radical.** S. V. Lebedev and N. A. Kudrjavtzev (J. Gen. Chem. Russ., 1935, **5**, 1859—1865).—In presence of floridin $CHBu^{\gamma}{:}CH_2$ is converted into $CMe_2{:}CMe_2$ (I) (160—170°), and $CHBu^{\gamma}{:}CHMe$ into $CMe_2{:}CMeEt$ (II) (150—270°), whilst (I), (II), and $CBu^{\gamma}{\vdots}CH$ (145—360°) are unaffected. R. T.

**Determination of piperylene by means of maleic anhydride.** V. P. Krause, A. M. Kogan, and M. A. Polievktova (Sintet. Kautschuk, 1934, No. 3, 30—33).—Piperylene with maleic anhydride (I) forms 3-methyl-$\Delta^4$-tetrahydrophthalic anhydride and rubber-like polymerides. The reaction is carried out in a weighed sealed flask for 30 min. at 70—75°, the product which is non-volatile in vac. at room temp. being weighed. Excess of (I) decreases the formation of polymeride. Ch. Abs. (*e*)

**Determination of diallyl and dipropenyl in their mixtures by the hydrogenation method.** J. M. Slobodin (J. Gen. Chem. Russ., 1935, **5**, 1830—1832).—Dipropenyl (I) undergoes hydrogenation only after complete saturation of diallyl (II); the composition of (I)–(II) mixtures can be determined from velocity of hydrogenation data. R. T.

**Dimerisation of $\Delta^{\alpha\gamma}$-butadiene.** S. V. Lebedev and S. R. Sergienko (J. Gen. Chem. Russ., 1935, **5**, 1839—1858).—Divinyl is converted into $\Delta^3$-*cyclo*hexenylethylene (I) by heating at 150° for 120 hr.; (I) yields cis-, m.p. 74—75°, and trans-3 : 4-*dibromo*-1-*αβ-dibromoethyl*cyclo*hexane*, m.p. 101·5°, and *α-bromoethyl*-, b.p. 102—104°/20 mm., and *αβ-dibromoethyl*-$\Delta^3$-cyclo*hexene*, b.p. 105—118°/3 mm., with Br in $Et_2O$ at 0°. (I) is very gradually converted at 150° into $\Delta^1$-*cyclo*hexenylethylene. R. T.

**Raman effect and organic chemistry. Allyl isomerism in the case of the bromohexenes.** (Mlles.) H. van Risseghem and B. Gredy (Compt. rend., 1936, **202**, 489—491).—$PBr_3$ and propylvinylcarbinol give $CHPrBr{\cdot}CH{:}CH_2$ (I) and $CHPr{:}CH{\cdot}CH_2Br$ (II), separated by distillation under reduced pressure. Isomerisation of (I) and (II) into an equilibrium mixture [90—95% (II)] occurs on repeated distillation at 100° in a sealed tube, and was followed by means of the Raman lines near 1650 $cm.^{-1}$ characteristic of the double linking. The isomerisation of (I) and (II) explains the formation of the same mixture from either of the corresponding alcohols. H. G. M.

**Bromides obtained by action of phosphorus tribromide on propylvinylcarbinol, and the corresponding acetates.** (Mlles.) B. Gredy and H. van Risseghem (Bull. Soc. chim. Belg., 1936, **45**, 177—185).—Propylvinylcarbinol with $PBr_3$ in $C_5H_5N$ below 0° affords trans-*α-bromo-$\Delta^{\beta}$-hexene* (I), b.p. 57·5—58°/25 mm., and *γ-bromo-$\Delta^{\alpha}$-hexene* (II), b.p. 51—52°/36 mm. On keeping (I) passes partly into (II) (cf. A., 1935, 1480; also preceding abstract). (I) with NaOAc affords *trans*-$\Delta^{\beta}$-hexenyl acetate (III) (cf. A., 1928, 1112), whilst (II) gives a mixture of *γ-acetoxy-$\Delta^{\alpha}$-hexene*, b.p. 49—50°/16 mm., and (III). Either Ac derivative is stable at 100°. J. L. D.

**Alkylacetylenes and their additive compounds. IX. Reaction of allyl bromide with acetylenic Grignard reagents.** J. P. Danehy, D. B. Killian, and J. A. Nieuwland (J. Amer. Chem. Soc., 1936, **58**, 611—612).—$CH_2{:}CH{\cdot}CH_2{\cdot}C{\vdots}CR$ (I) could not be prepared from $CH_2{:}CH{\cdot}CH_2Br$ (II) and $CR{\vdots}C{\cdot}MgX$ in $Et_2O$, $C_6H_6$, or di-*n*-amyl ether; reaction occurs, however, in presence of anhyd. $Cu_2Cl_2$ or $Cu_2Br_2$, and to a smaller extent with $Cu_2(CN)_2$ or $CuHal_2$. Cu-bronze, $Cu_2S$, and CuS are not catalysts. Vinyl- [(I) $R=CH_2{:}CH{\cdot}$], b.p. 109—110°/750 mm. (explodes violently on attempted combustion), *butyl*-, b.p. 58°/22 mm., amyl-, b.p. 73—74°/22 mm., and phenyl-, b.p. 107—108°/22 mm., -allylacetylenes are described. *β-Methyl-$\Delta^{\gamma}$-octinen-β-ol*, b.p. 92—93°/33 mm., is formed from $COMe_2$ and $CBu{\vdots}C{\cdot}MgBr$ even in presence of (II). H. B.

**Trifluoronitrosomethane, $CF_3{\cdot}NO$. III.** O. Ruff and M. Giese (Ber., 1936, **69**, [*B*], 684—689).—

The production of trifluoronitrosomethane by the action of F on technical AgCN is due to the presence of $AgNO_3$ or, possibly, $Ag_2O$; the best yields are obtained from $AgCN–CaF_2–KNO_3–Ag_2O$ (1 : 2 : 0·3 : 0·3). The blue fraction, formerly regarded as homogeneous $CF_3\cdot NO$, corresponds in all portions according to mol. wt. and analyses with the at. ratio $CF_3NO$. It has b.p. −84°, m.p. −196·6°. The gas is unchanged in contact with glass, 96% $H_2SO_4$, 60% $HNO_3$, 35% HCl, Hg, AcOH, $K_2Cr_2O_7$, $CrO_3$–AcOH, $HSO_4$, $KMnO_4$ with 10% $H_2SO_4$ or AcOH, $H_2O_2$, or $H_2S$, but becomes decolorised in presence of 8% NaOH, active C, $Mn_2O_7$ in AcOH, Zn dust and AcOH, Pd-sponge and dil. HCl. It therefore contains about 50—48% of the colourless isomeride $COF\cdot NF_2$ which is so stable that the chemical properties of the blue fraction are almost identical with those of homogeneous $CF_3\cdot NO$. H. W.

**Chlorofluoroethanes and chlorofluoroethylenes. II.** A. L. Henne and E. C. Ladd. **III.** A. L. Henne and D. M. Hubbard (J. Amer. Chem. Soc., 1936, **58**, 402—403, 404—406; cf. A., 1934, 1089).—II. The prep. of the following *compounds* is described: $CHCl_2\cdot CCl_2F$, m.p. −82·6°, b.p. 116·6°; $CHClF\cdot CCl_3$, m.p. −95·35°, b.p. 117·0°; $CHCl_2\cdot CClF_2$, b.p. 71·9°; $CHClF\cdot CCl_2F$, b.p. 72·5°; $CHF_2\cdot CCl_3$, b.p. 73·0°; $CHClF\cdot CF_2Cl$, b.p. 28·0°; $CHF_2\cdot CF_2Cl$, b.p. −12°; $CHF:CCl_2$, m.p. −108·8°, b.p. 37·3°; $CHCl:CClF$, b.p. 35·1°; $CHCl:CF_2$, b.p. 2·4°; $CHClBr\cdot CClFBr$, b.p. 163·5°; $CHClBr\cdot CF_2Br$, b.p. 118·7°. The preferential course of fluorination during synthesis is discussed.

III. Fluorination of $CH_2Cl\cdot CCl_3$ with $SbF_3$ gives αββ-*trichloro*-β-*fluoroethane*, m.p. −104·7°, b.p. 88·0°, and αβ-*dichloro*-ββ-*difluoroethane*, m.p. −101·2°, b.p. 46·8°. E. S. H.

**Preparation of *n*-heptyl bromide.** C. L. Tseng, T. S. Ho, and (Miss) P. T. Chia (Sci. Rep. Nat. Univ. Peking, 1936, **1**, 17—18).—$HBr–H_2SO_4$, $NaBr–H_2SO_4$, and $PBr_3$ give 66—69, 60·4, and 64·5%, respectively, of $n\text{-}C_7H_{15}Br$. R. S. C.

**Hydroxyl linking in *n*-aliphatic alcohols.** D. A. Wilson (Nature, 1936, **137**, 617—618).—A discussion. L. S. T.

**Hydrogen linking between oxygen atoms in organic compounds.** G. E. Hilbert, O. R. Wulf, S. B. Hendricks, and U. Liddel (J. Amer. Chem. Soc., 1936, **58**, 548—555; cf. A., 1935, 563).—The following compounds give no infra-red absorption characteristic of mols. containing the OH group: $CH_2Ac_2$, $CH_2BzAc$, $CH_2Bz_2$, $o\text{-}OH\cdot C_6H_4\cdot CHO$, *p*-homosalicylaldehyde, Me and Ph salicylates, Me 3 : 5-dibromosalicylate, $o\text{-}OH\cdot C_6H_4\cdot COMe$, 2 : 1-$C_{10}H_6Ac\cdot OH$, 1 : 2-$C_{10}H_6Bz\cdot OH$, 2-hydroxy-5-methylbenzophenone, dihydrorotenol, 1-hydroxyanthraquinone, $o\text{-}OH\cdot C_6H_4\cdot CO\cdot NH_2$, $o\text{-}NO_2\cdot C_6H_4\cdot OH$, 2 : 6-$(NO_2)_2C_6H_3\cdot OH$, 1 : 2-$NO_2\cdot C_{10}H_6\cdot OH$, 1 : 4-, 1 : 5-, and 1 : 8-dihydroxyanthraquinones, 5 : 8-dihydroxy-1 : 4-naphthaquinone, naphthazarin, 2 : 4- and 4 : 6-diacetyl- and -dinitro-resorcinols, 2-nitroresorcinol, 2 : 2′-dihydroxy-1 : 1′-dinaphthyl sulphone, 2 : 2′-dihydroxybenzophenone, derritol, and Et 2 : 5-dihydroxyterephthalate. The above compounds are chelated (singly or doubly) through H. The following show OH absorption (which often differs from that of simple alcohols) and are not, therefore, chelated: aldol, α- and β-benzilmonoximes, benzoin, α- and β-benzoinoxime acetates, Et and Buᵅ *d*-tartrates, *Et mesotartrate*, $o\text{-}C_6H_4(OH)_2$, and $o\text{-}C_6H_4Cl\cdot OH$. 9-Keto-10-nitromethyl-9 : 10-dihydro-10-phenanthrol is considered not to contain a H linking. 3-Nitropyrocatechol appears to contain a single chelate linking (cf. Baker, A., 1935, 85). Et 3 : 6-dibromo-2 : 5-dihydroxyterephthalate (I) is probably not chelated; the $CO_2Et$ groups are probably displaced owing to the proximity of the Br. A structure is suggested for (I); it indicates the possibility of *cis*- and *trans*-forms of (I) and resolution of, *e.g.*, alkyl 3-bromo-4- or -5-aminosalicylates. H. B.

**Reaction products of ethyl alcohol and sodium hydroxide.** D. Williams and R. W. Bost (J. Chem. Physics, 1936, **4**, 251—253).—NaOH and EtOH when heated in the absence of $H_2O$ form NaOEt and $H_2O$, which latter can be detected by means of its absorption band at 4·7 μ, by the Cu acetylide method, and by its reaction with $CaC_2$. The reaction goes to 75—100% completion. L. J. J.

**Mechanism of contact conversion of alcohols into diethylenic hydrocarbons by the method of S. V. Lebedev.** J. A. Gorin and O. M. Neimark (J. Gen. Chem. Russ., 1935, **5**, 1772—1780).—The chief product obtained when PrOH is passed over a mixed dehydrating–dehydrogenating catalyst (not specified) at 400° is $CH_2:CMe\cdot CH:CHMe$; $CHMe:CH_2$, EtCHO, $CMe_2:CHEt$, *iso*hexane, and $H_2$ are obtained as by-products. R. T.

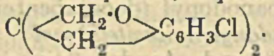
**Highly unsaturated alcohols in sperm blubber oil.** Y. Toyama and G. Akiyama (Bull. Chem. Soc. Japan, 1936, **11**, 29—34).—The high-boiling fraction of the unsaponifiable matter of the oil contains clupanodonyl (docosapentenol; A., 1926, 1226) and *catadonyl* (*eicositetraenol*; $Br_8$-, blackens at about 240°, and *Ac* derivatives) alcohols. The latter is hydrogenated to *n*-eicosanol. H. G. M.

**Hydrogenation of acetylene derivatives. XXIII. Dihexylbutinenediol.** J. S. Salkind [with V. I. Tzereschko] (J. Gen. Chem. Russ., 1935, **5**, 1768—1771).—Two *isomerides* of $(Me\cdot[CH_2]_5\cdot CH(OH)\cdot C:)_2$ are described, (I), m.p. 47—49°, and (II), m.p. 68—70°. (I), when hydrogenated (Pd), yields two *isomerides* of $(Me\cdot[CH_2]_5\cdot CH(OH)\cdot CH:)_2$, one (III), m.p. 44—45°, and the other (IV) an oil, b.p. 195—200°/14 mm. (*dibromide*, m.p. 140°); (III) gives *hexadecane*-ηκ-*diol* (V), m.p. 85—86°, and (IV) an *isomeride* (VI) of (V), m.p. 105—106°, when further hydrogenated. The dibromide, m.p. 97—98°, obtained from the mixture of (I) and (II) eliminates Br when treated with Zn in EtOH, to yield a *product* (VII), m.p. 53—54°, isomeric with (II). It is concluded that (I) is a mixture of optical (?) isomerides, and that hydrogenation proceeds as follows: (VII) → (III) → (V); (II) → (IV) → (VI). R. T.

**Catalytic action of monoses on the condensation of aldehydes. II. Synthesis of pentaerythritol.** A. Kuzin (J. Gen. Chem. Russ. 1935

5, 1527—1529).—Glucose or fructose catalyses the condensation of $CH_2O$ and MeCHO to pentaerythritol. R. T.

**Isomeric monoalkyl ethers of β-methylpropane-αβ-diol from αβ-epoxy-β-methylpropane.** C. E. Sparks and R. E. Nelson (J. Amer. Chem. Soc., 1936, 58, 671—672).—αβ-Epoxy-β-methylpropane (I) (1 mol.) with 3 mols. of MeOH, EtOH, and $Pr^aOH$ (rate of reaction and yield diminish in this order) at 230—270° under pressure give $OAlk·CMe_2·CH_2·OH$ [Alk=*$Pr^a$* (II), b.p. 162—163°/739·2 mm.] and $OH·CMe_2·CH_2·OAlk$ [Alk=$Pr^a$, b.p. 147—147·5°/748·6 mm. (lit. 150—151°/763 mm.)]. (I) heated with $Pr^aOH$ and 10% $H_2SO_4$ affords (II). H. B.

**Radiate ethers of pentaerythritol.** H. J. Backer and G. Dijkin (Rec. trav. chim., 1935, 55, 22—32).—The prep. of the following *pentaerythritol ethers* is described: $Me_4$ (I), m.p. 30—30·5°, b.p. 196—198°; $Et_4$, b.p. 230—231°/763 mm. (cf. lit.); $Pr^a_4$, b.p. 124—127°/3 mm.; $Bu^\gamma_2$, m.p. 102—104°; *tetracetyl*, m.p. 57·5—59°; $Ph_4$ (II), m.p. 113—113·5° [$(NO_2)_8$-derivative, decomp. about 114°]; *tetra*-p-*bromophenyl* (III), m.p. 153—157° (crystallises from $C_6H_6$–$CHCl_3$ with 2 mols. of $C_6H_6$), also obtained by bromination of (II); *tetra*-p-*chlorophenyl* (IV), m.p. 141—142°; *tetra*-p-*tolyl* (V), m.p. 96°; $(CH_2Ph)_4$, b.p. 246—250°; *tetra*-p-tert.-*butylphenyl*, m.p. 168—169° ($Br_4$-derivative, m.p. 231—232°); *tetra*-p-tert.-*amylphenyl*, m.p. 193—194·5°; $(\alpha\text{-}C_{10}H_7)_4$, m.p. 170—171·5° (*monopicrate*, m.p. 200—201·5°); $(\beta\text{-}C_{10}H_7)_4$, m.p. 119—120° (*dipicrate*, m.p. 189·5—190·5°). (II) when boiled with $AlCl_3$ in $C_6H_6$ is converted into an *isomeride*, m.p. 97—98°, also obtained when $C(CH_2Br)_4$ is heated with PhOH and Na. This does not react with AcCl or dissolve in alkali; its $(NO_2)_8$-derivative, decomp. about 115°, however, is readily sol. in $COMe_2$ and in KOEt–EtOH. (IV) when heated with $AlCl_3$ in light petroleum gives a *compound*, m.p. 218—220°, considered to be  $C\left(<\begin{matrix}CH_2·O\\CH_2\end{matrix}>C_6H_3Cl\right)_2$. A similar *compound*, m.p. 169—170°, is obtained from (V) with $AlCl_3$, and is also formed from $C(CH_2Br)_4$, Na, and *p*-cresol together with an *isomeride*, m.p. 100·5—101·5°, of (V). The crystallographic properties of (I)—(V) have been determined (by P. Terpstra). H. G. M.

**Syntheses of glycerides by means of triphenylmethyl compounds. II. Diglycerides.** P. E. Verkade and J. van der Lee (Rec. trav. chim., 1936, 55, 267—277).—α-Monostearin (I) and $CPh_3Cl$ in quinoline afford *γ-triphenylmethylglyceryl α-stearate* (II), m.p. 66·5—67°, and *βγ-ditriphenylmethylglyceryl α-stearate*. Similarly, α-monopalmitin affords *γ-triphenylmethylglyceryl α-palmitate* (III), m.p. 61·5—62°. (II) and γ-triphenylmethylglyceryl αβ-distearate are also obtained from triphenylmethylglycerol and stearyl chloride (IV). Palmityl chloride and (II) give *γ-triphenylmethylglyceryl β-palmitate α-stearate* (V), m.p. 37—37·5°, and (III) and (IV) give *γ-triphenylmethylglyceryl α-palmitate β-stearate* (VI), m.p. 57—57·5°. Removal of $CPh_3$ from (V) and from (VI) affords glyceryl α-stearate γ-palmitate. P. G. C.

**Constituents of the adrenal gland. III. Sulphur-containing substance.** T. Reichstein and A. Goldschmidt (Helv. Chim. Acta, 1936, 19, 401—402; cf. this vol., 605).—$S(CH_2·CH_2·OH)_2$ with 27% $H_2O_2$ (1 mol.) in a little AcOH gives *di-β-hydroxyethyl sulphoxide* (I), m.p. 112—113° (corr.) (reduces $KMnO_4$ at 0° instantaneously), identical with the substance isolated from the adrenal gland. Solubility relations show that (I) occurs naturally as ester of a fatty acid. Possibly, however, the SO is produced during isolation. R. S. C.

**Thio-derivatives of glycerol. I. Preparation of α-monothioglycerol.** L. Smith and B. Sjöberg (Ber., 1936, 69, [*B*], 678—680).—βγ-*iso*Propylidenedioxypropyl chloride is converted by $K_2S_2$ at 100° into *di-βγ-*iso*propylidenedioxypropyl disulphide*, b.p. 165°/3 mm., which is hydrolysed by 2·5*N*-$H_2SO_4$ and then electrolytically reduced at a Pb electrode to *α-thiolpropane-βγ-diol* [*α-monothioglycerol*], b.p. 112°/3 mm. Essentially the same substance appears to result from βγ-oxidopropyl alcohol and $H_2S$ in presence of $Ba(OH)_2$ at room temp. H. W.

**β-Oxidation and ω-oxidation.** B. Flaschenträger and K. Bernhard (Rec. trav. chim., 1936, 55, 278—281).—A reply to Verkade *et al.* (this vol., 234). P. G. C.

**ψ-Halogens. XXXII. Reaction of the silver salts of monobasic organic acids with iodine in the presence of benzene.** L. Birckenbach and K. Meisenheimer (Ber., 1936, 69, [*B*], 723—729).—The possible actions between I and the Ag salts of monobasic org. acids in presence of $C_6H_6$ are represented: $R·CO_2Ag+I_2 \rightleftharpoons R·CO_2I+AgI$; $R·CO_2I+C_6H_6 \longrightarrow$ (*a*) $PhI+R·CO_2H$ or (*b*) $ROBz+HI$; $HI+R·CO_2Ag=R·CO_2H+AgI$; $R·CO_2I+R·CO_2Ag \rightleftharpoons [R·CO_2I,AgO_2C·R] \longrightarrow$ (*c*) $R·CO_2R+CO_2+AgI$. With aliphatic acids reaction (*c*) is so much more rapid than (*a*) or (*b*) that substitution occurs to only a slight extent, if at all. With BzOH the reactions are about equally rapid, whereas with substituted benzoic acids substitution is so much the faster process that only a slight evolution of $CO_2$ is observed. With aliphatic acids change (*b*) does not occur appreciably except in the case of AcOH. With AgOBz approx. equal amounts of PhI and PhOBz are formed, but the latter may arise according to (*c*). Among the isomeric nitro-, chloro-, and methylbenzoic acids the *p*-derivatives followed by the *m*-compounds react most markedly according to (*b*), the *o*-derivatives exclusively in accordance with (*a*). The results appear related to the electrolytic dissociation consts. of the acid. The action of $Cl_2$ or Br on $p$-$C_6H_4Cl·CO_2Ag$ in $C_6H_6$ is examined in cold solution in the dark; it takes place without evolution of $CO_2$, giving mainly PhCl and PhBr, respectively, with 0% and 6% of Ph ester. Substitution of PhCl for $C_6H_6$ in the reaction of $p$-$C_6H_4Cl·CO_2Ag$ and I considerably diminishes the rate of substitution (recognisable by increased evolution of $CO_2$) without influencing the ratio of changes (*a*) and (*b*), whereas PhOMe enhances substitution and a complete displacement towards direction (*a*). H. W.

**Preparation of cellulose acetate. I. Preparation of acetyl chloride.** Y. Kato and S. Fujino

(J. Electrochem. Assoc. Japan, 1935, **3**, 42—46).—$Cl_2$ is passed into a mixture of $PCl_3$ and AcOH.

Ch. Abs. (*r*)

**Products of reaction of ethyl dichloroacetate with alcoholic sodium ethoxide.** A. C. Cope (J. Amer. Chem. Soc., 1936, **58**, 570—572).—Contrary to Wohl and Lange (A., 1908, i, 943), $CHCl_2{\cdot}CO_2Et$ (I) (1 mol.) and EtOH–NaOEt (1·5 mols.) give 22% of $CH(OEt)_2{\cdot}CO_2Et$ (II), b.p. 84—85°/14 mm., and 42% of *Et α-chloro-ββ-diethoxysuccinate* (III), b.p. 122—125° (slight decomp.)/2 mm. (III) heated at 170—250° affords CO, $CO_2$, $C_2H_4$, small amounts of $HCO_2Et$, $Et_2CO_3$, and EtOH, 23% of $CHCl(CO_2Et)_2$, and 58% of *Et α-chloro-β-ethoxymaleate*, b.p. 150—152°/17 mm. [free *acid* ($+H_2O$), m.p. 77—77·5°, m.p. (anhyd.) 88—88·5° (*anhydride*, m.p. 37—37·5°)]. (III) is hydrolysed by aq. EtOH–HCl (trace) to $Et_2$ oxalochloroacetate. (III) is not obtained from $OEt{\cdot}CHCl{\cdot}CO_2Et$ and EtOH–NaOEt or from (I), (II), and EtOH–NaOEt. (III) may arise thus:

$$2CHCl_2{\cdot}CO_2Et \longrightarrow ({:}CCl{\cdot}CO_2Et)_2 \xrightarrow{EtOH} CO_2Et{\cdot}CHCl{\cdot}CCl(OEt){\cdot}CO_2Et \xrightarrow{NaOEt} CO_2Et{\cdot}CHCl{\cdot}C(OEt)_2{\cdot}CO_2Et.$$

H. B.

**Grignard reactions with ethyl β-chloropropionate. I.** C. Weizmann and E. Bergmann (J.C.S., 1936, 401—402).—MgRBr and MgRCl with $CH_2Cl{\cdot}CH_2{\cdot}CO_2Et$ give, respectively, $CH_2Cl{\cdot}CH{:}CR_2$ and $CH_2Cl{\cdot}CH_2{\cdot}CR_2{\cdot}OH$ which with KOH yields $CH_2{:}CH{\cdot}CR_2{\cdot}OH$. The following new *carbinols* were prepared: *dibenzyl-β-chloroethyl-*, b.p. 214°/22 mm., 206°/8 mm., 192°/3 mm.; *dibenzylvinyl-*, b.p. 145—146°/1 mm., reduced ($Pd–BaSO_4$) to *dibenzylethyl-*, b.p. 190—192°/12 mm. [also prep. from $CO(CH_2Ph)_2$ and MgEtBr], *dibenzyl-β-piperidinoethyl-*, b.p. 224—225°/5 mm., m.p. 45—46° (p-*nitrobenzoate*, m.p. 138—139°; p-*aminobenzoate*, b.p. 245—250°/25 mm., m.p. 147—148°), *β-chlorotriethyl-*, b.p. 118—119°/54 mm., β-piperidinotriethyl-, b.p. 105—106°/3 mm. [p-*nitrobenzoate*, m.p. 148° (*alcoholate*, m.p. 100°; *hydrochloride*, cryst.)], *β-chloroethyldibutyl-*, b.p. 128—133°/4 mm., *dibutylvinyl-*, b.p. 125°/34 mm., *β-piperidinoethyldibutyl-*, b.p. 140—143°/5 mm. MgPhBr with $CH_2Cl{\cdot}CH_2{\cdot}CO_2Et$ gives *γγ-diphenylallyl chloride*, b.p. 159—161°/4 mm. (converted by MgPhBr into $CPh_2{:}CH{\cdot}CH_2Ph$), and $CH_2Cl{\cdot}CH_2{\cdot}COPh$, identified as $CH_2Ph{\cdot}CH_2{\cdot}COPh$. F. R. G.

**Comparison of a group of isomeric ethylenic chlorides (allyl–crotonic isomerism) amongst themselves and with the corresponding bromides, on the basis of reactions and mobility of hydrogen.** R. Rambaud (Bull. Soc. chim., 1936, [v], **3**, 134—141).—Et γ-chlorocrotonate (I) (improved prep.) reacts with hot and cold solutions of alkalis, alkali acetates, $NH_3–H_2O$ [product isolated was the *picrate*, m.p. 130—150° (decomp.), of γ-aminocrotonic acid], and alkaline-earth iodides, giving the same products as are obtained from the γ-Br-compound (cf. A., 1935, 63, 64). The reaction with NaOEt is an exception (*ibid.*, 1105). (I) reacts about twice as rapidly as Et α-chloro-$\Delta^{\beta}$-butenoic acid (II) with NaI in $COMe_2$, whereas Et α-chlorocrotonate does not react. (II) is oxidised by AgOH probably to *$Et_2$ αα′-dichloro-αα′-divinylsuccinate*. H. G. M.

**Geometrical isomerism of halogen-substituted ethylenic acids. Synthesis of β-bromo-$\Delta^{\alpha}$-pentenoic acids.** A. E. Favorski and V. O. Mochnatsch (J. Gen. Chem. Russ., 1935, **5**, 1668—1678).—$CEt{:}C{\cdot}CO_2H$ (I) (*K*, $+2H_2O$, *Na*, $+2H_2O$, *Ca*, $+0{\cdot}5H_2O$, *Sr*, $+1{\cdot}5H_2O$, *Mg*, $+3H_2O$, *Ba*, $+0{\cdot}5H_2O$, salts), obtained by boiling a paraffin solution of αβ-dibromobutane with $NaNH_2$ and saturating the product with $CO_2$, reacts with aq. HBr at 0° to yield two *stereoisomerides* of $CEtBr{:}CH{\cdot}CO_2H$ (II), one, m.p. 24—26° (*K*, $+2H_2O$, and *Ca* salts), and the other, m.p. 53·5—54° (*K*, $+H_2O$, *Ba*, $+0{\cdot}5H_2O$, and *Ca*, $+4H_2O$, salts). α-Bromovaleric acid, b.p. 109·5—110·5°/6·5 mm. (lit. 67°/10 mm.) (*Na*, $+0{\cdot}5H_2O$, *Ca*, $+7H_2O$, *Mg*, $+H_2O$, and *Sr*, $+H_2O$, salts), and Br (145—160°; 6 hr.) yield *αα-dibromovaleric acid*, b.p. 118—128°/10 mm., converted by steam-distillation into *α-bromo-$\Delta^{\alpha}$-pentenoic acid*, b.p. 113—115°/5 mm. (*Ca*, *Ba*, and *K* salts). Both forms of (II) regenerate (I) when heated with aq. $Ba(OH)_2$. R. T.

**Decenoic acid $C_{10}H_{18}O_2$ in sperm head oil.** Y. Toyama and T. Tsuchiya (Bull. Chem. Soc. Japan, 1936, **11**, 26—29).—The isolation of $\Delta^{\theta}$-decenoic acid from sperm head oil is described. Its constitution is established by hydrogenation to decoic acid and by oxidation of the Me ester in $COMe_2$ by $KMnO_4$ to azelaic and formic acids. H. G. M.

**Transposition of the double linking in $\Delta^{\epsilon}$- and $\Delta^{\iota}$-oleic acids.** I. I. Vanin and A. A. Tschernojarova (J. Gen. Chem. Russ., 1935, **5**, 1537—1542).—$\Delta^{\iota}$-Oleic acid in AcOH and HCl at 0° yield ι-chlorostearic acid, which with $NiCO_3$ (190—210°; 3 hr.) affords *iso*oleic acid, $Me{\cdot}[CH_2]_6{\cdot}CH{:}CH{\cdot}[CH_2]_8{\cdot}CO_2H$, m.p. 43—44°. $\Delta^{\epsilon}$-Oleic acid and HCl yield ζ-chlorostearic acid, converted similarly into $Me{\cdot}[CH_2]_9{\cdot}CH{:}CH{\cdot}[CH_2]_5{\cdot}CO_2H$, m.p. 51—52°.

R. T.

**Halogenation of the thiocyanates of polyethylenic acids. Synthesis of halogenothiocyanates of ethyl linoleate.** W. Kimura (Ber., 1936, **69**, [*B*], 786—789).—Et linoleate is obtained by the successive action of Zn dust and conc. $H_2SO_4$ on tetrabromostearic acid in abs. EtOH. It is converted by $(CNS)_2$ in $CCl_4$ into *Et θι-dithiocyano-$\Delta^{\lambda}$-octadecenoate*, which with $Cl_2$ or Br respectively in cold $Et_2O$ affords *Et λμ-dichloro-* and *λμ-dibromo-θι-dithiocyanostearate*. With Wijs' and Hanns' solutions *Et λμ-chloroiodo-* and *λμ-bromoiodo-θι-dithiocyanostearate* result. H. W.

**Polymerisation of the methyl esters of higher unsaturated fatty acids. XVII. Increase in the iodine value of the polymerisation product.** K. Kino (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, **29**, 31—36; cf. A., 1934, 755).—The Me esters of the fatty acids of linseed and sesamé oil, and Me oleate show no increase in I val. even after being in contact with I during 24 hr., but after heating at 280—290° for several hr. the increase may amount to 16·7 units, and is the higher the greater is the unsaturation of the starting material. Intermol. polymerides, unhydrolysable substances derived from them, and substances of high b.p. are responsible for the increase. Some substitution occurs in the polymerisation product, but the reaction is mainly additive. J. L. D.

**Interaction between the methyl esters of unsaturated aliphatic acids of the $C_{20}$ and $C_{22}$ class, containing four and five ethenoid linkings respectively, and maleic anhydride.** R. S. Morrell and W. R. Davis (J.S.C.I., 1936, **55**, 101—103T).—The Diels–Alder synthesis between conjugated diene systems and maleic anhydride has been extended to the Me esters of unsaturated $C_{20}$ and $C_{22}$ acids occurring in fish oils. No reaction of the type was found with either of these esters, although the former contained four and the latter five ethenoid linkings, respectively. The absence of conjugation indicated by these results is in accordance with existing work on the structure of the acids. An impurity in the $C_{20}$ ester produced a small amount of amorphous heteropolymeride, probably composed of an oxidised pentaethylenic mol. in combination with three mols. of anhydride.

**Lead complexes of hydroxy-acids.** H. Pariselle (Compt. rend., 1936, **202**, 1173—1176).—Pb tartrate exists in two forms; the hydrated salt first pptd. has an acid reaction, but changes subsequently into an anhyd. neutral form. The action of aq. NaOH on an equimol. mixture of tartaric acid and $Pb(NO_3)_2$ has been followed polarimetrically. The ppt. first obtained redissolves in excess of NaOH, giving a *l*-complex in solution. The rotatory power is a function of [NaOH], becoming positive and then negative again as this increases. With aq. $NH_3$ the solution always remains *l*. A comparison with the behaviour of Pb saccharate in aq. KOH is made. The *l*-complex first produced becomes *d* as [KOH] increases, but there is no return to *l* with further increase of [KOH]. M. S. B.

**Determination of keto–enolic mixtures.** F. Seidel, W. Thier, A. Uber, and J. Dittmer (Ber., 1936, **69**, [*B*], 650—653).—In presence of $OAc\cdot CMe\colon CH\cdot CO_2Et$ the enolic fraction of $CHAc_2\cdot CO_2Et$ can be determined by titration with $0\cdot 2N$-NaOH or -$Ba(OH)_2$ in presence of phenolphthalein, since $OAc\cdot OMe\colon CH\cdot CO_2Et$ does not react appreciably with alkali. The results agree with those of Meyer's Br titration. The % enol in $CHAc_2$ can be similarly determined, but the procedure fails with $CH_2Ac\cdot CO_2Et$. H. W.

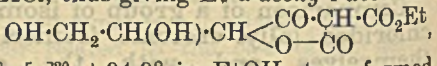
**Acetolic condensations of ethyl acetoacetate with acetaldehyde.** H. Gault and T. Wendling (Bull. Soc. chim., 1936, [v], **3**, 53—70; cf. A., 1935, 65).—$CH_2Ac\cdot CO_2Et$, MeCHO, $K_2CO_3$, and $H_2O$ give Et di-α′-hydroxyethylacetoacetate (I) and an oil consisting of $Et_2$ ethylidenebisacetoacetate and some $Et_2$ dimethyl*cyclo*hexenonedicarboxylate, or of Et α′-hydroxyethylacetoacetate, according to the temp. at which it was separated. $NHEt_2$ or KOH may be used instead of $K_2CO_3$ in the prep. of (I), but the $H_2O$ cannot be replaced by EtOH. The stability of (I) at various temp. in the pure state and in $H_2O$, EtOH, and $Et_2O$ is recorded. H. G. M.

**Preparation of macrocyclic lactones by depolymerisation.** E. W. Spanagel and W. H. Carothers (J. Amer. Chem. Soc., 1936, **58**, 654—656).—The polyesters from $OH\cdot[CH_2]_n\cdot CO_2H$ ($n=9$, 12, 13) and $OH\cdot[CH_2]_n\cdot O\cdot[CH_2]_{10}\cdot CO_2H$ ($n=2$—4) are depolymerised at 270°/1 mm. in presence of (usually) a little $MgCl_2,6H_2O$ to the mono- (main product with higher members) and/or di-meric lactones; this method (cf. A., 1935, 844) is simpler and quicker than that of Stoll and Rouvé (A., 1934, 1201; 1935, 1351). The following are new: κ-β′-*hydroxyethoxyundeco-mono-* (I), b.p. 108—111°/1 mm., m.p. 8°, and *-di-*, m.p. 106—107°, *-lactones*; κ-δ′-*hydroxybutoxyundecomonolactone* (II), b.p. 129—131°/1 mm., m.p. −19°. (I) and (II) have musk-like odours. κ-β′-*Hydroxyethoxy-*, m.p. 48—50°, κ-γ′-*hydroxypropoxy-*, m.p. 51°, and κ-δ′-*hydroxybutoxy-*, m.p. 53°, *-undecoic acids* are prepared from κ-bromoundecoic acid and $OH\cdot[CH_2]_n\cdot ONa$ in $(CH_2)_n(OH)_2$. The effects of temp. and catalyst on the depolymerisation are studied. H. B.

**Autoxidation of fatty acids. II. Oxidoelaidic acid and some cleavage products.** G. W. Ellis (Biochem. J., 1936, **30**, 753—761; cf. A., 1932, 931).—The rate of autoxidation of elaidic acid (I) has been increased to an $O_2$ uptake of 20% in < 7 hr. $CO_2$ must be removed by rapid circulation of $O_2$, and 0·2% of Co, as elaidate, be added. *Oxidoelaidic acid*, m.p. 55·5°, is formed to the extent of 16·20% of (I) oxidised. A similar oxidation of oleic acid yielded 20% of the same acid with a small amount of oxido-oleic acid. Autoxidation of (I) also yields azelaic, suberic, nonoic, and octoic acids, and a trace of $H_2C_2O_4$. J. N. A.

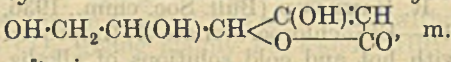
**Micrometric oxalic acid titration.** J. Renaudin (J. Pharm. Chim., 1936, [viii], **23**, 447—454).—Micrometric titration of $H_2C_2O_4$ with $KMnO_4$ by the usual procedure using hot solutions is not trustworthy. Cold titration with $0\cdot 01N$-$Na_2S_2O_3$ after addition of excess of $0\cdot 01N$-$KMnO_4$ and KI is more accurate. Addition of $MnSO_4$ accelerates the liberation of I and is desirable in the presence of mineral salts. E. H. S.

**α-Deoxy-*l*-ascorbic acid.** F. Micheel and K. Hasse (Ber., 1936, **69**, [*B*], 879—881).—*iso*Propylideneascorbic acid (improved prep.) is transformed into K α-acetyl-βγ-*iso*propylidenethreonate, which with $SOCl_2$ at room temp. affords α-*acetyl*-βγ-iso*propylidenethreonyl chloride*, b.p. 124—126°/14 mm. This is condensed with $CHNa(CO_2Et)_2$ in anhyd. $Et_2O$, and the product is boiled with EtOH and then hydrolysed with dil. HCl, thus giving Et α-*deoxy*-l-*ascorbic*-α-*carboxylate*,



$$OH\cdot CH_2\cdot CH(OH)\cdot CH{<}\begin{matrix}CO\cdot CH\cdot CO_2Et\\ O\text{—}CO\end{matrix},$$

m.p. 116—117°, $[\alpha]_D^{20}$ +94·9° in EtOH, transformed by NaOH–MeOH into α-*deoxy*-l-*ascorbic acid*,



$$OH\cdot CH_2\cdot CH(OH)\cdot CH{<}\begin{matrix}C(OH)\colon CH\\ O\text{———}CO\end{matrix},$$

m.p. 170° after softening. H. W.

**[Isolation of crystalline *d*-galacturonic acid from tobacco.]** F. Ehrlich (Ber., 1936, **69**, [*B*], 920).—A question of priority (cf. Collatz, this vol., 591). H. W.

**Walden inversion reactions of *d*-(+)α-*p*-toluenesulphonoxypropionic acid and amide and their derivatives.** C. M. Bean, J. Kenyon, and H. Phillips (J.C.S., 1936, 303—311).—α-*p*-Toluenesulphonoxypropionic acid is partly resolved through tho quinine salt, but the optically pure acid is obtained from *d*-lactic acid. The *d*-(+)acid and $SOCl_2$ give d-(+)α-p-*toluenesulphonoxypropionyl chloride*, b.p.. 140—145° < 0·1 mm., m.p. 53°, $[\alpha]_{5461}$ +3·69° in $C_6H_6$; the *l*-(−)chloride with LiCl in $COMe_2$ yields (+)α-chloropropionyl chloride, converted into Et (+)α-chloropropionate. *l*-(−)α-*p*-Toluenesulphonoxypropionamide and KOAc in EtOH give d-(+)α-*acetoxypropionamide*, b.p. 128—131° < 0·1 mm., m.p. 59—60°, $\alpha^{18}_{5461}$ +4·26°. Et *l*-(−)lactate, converted into the acid and treated successively with AcCl, $SOCl_2$, and $CH_2Cl_2$ and $NH_3$, yields l-(−)α-*acetoxypropionamide*, b.p. 104—105°/< 0·1 mm., m.p. 59—60°, $\alpha_{5461}$ −17·7°. *d*-(+)α-Toluenesulphonoxypropionamide with KOBz affords d-(+)α-*benzoyloxypropionamide*, m.p. 127—128°, $[\alpha]_{5461}$ +66·6° in EtOH, also obtained from Et *l*-(−)lactate. *l*-(−)α-*p*-Toluenesulphonoxypropionanilide (I) with KOAc leads to d-(+)α-*acetoxypropionanilide*, $[\alpha]_{5461}$ +12·7° in EtOH; the *l*-(−)compound, obtained from $NH_2Ph$ and (−)acetoxypropionyl chloride, has m.p. 121° and $[\alpha]_{5461}$ −12·2° in EtOH. *d*-(−)α-Benzoyloxypropionanilide, obtained from (I) and KOBz, has m.p. 160°, $[\alpha]_{5461}$ −12·0° in EtOH, and the *l*-(+)compound, m.p. 160°, $[\alpha]_{5461}$ +15·0° in EtOH, is prepared from Et *l*-(−)lactate, through l-(+)α-*benzoyloxypropionyl chloride*, b.p. 98° < 0·1 mm., $[\alpha]_{5461}$ +51·3°. β-Naphthylamine and *l*-(−)α-*p*-toluenesulphonoxypropionyl chloride give *l*-(−)α-p-*toluenesulphonoxypropiono*-β-*naphthalide*, m.p. 128°, $[\alpha]_{5461}$ −123·8° in EtOH.

*dl*-α-*p*-Toluenesulphonoxypropionyl chloride and Na *p*-toluenesulphonamide lead to dl-α-p-*toluenesulphonoxy*-N-p-*toluenesulphonylpropionamide*, m.p. 137°, and similarly *K* l-α-p-*toluenesulphonoxy*-N-p-*toluenesulphonylpropionamide*, m.p. 160° (decomp.), $[\alpha]_{5461}$ −79·4° in $COMe_2$, is derived. The K salt and EtOH yield l-(−)α-*ethoxy*-N-p-*toluenesulphonylpropionamide*, m.p. 80—81°, $[\alpha]_{5893}$ −10·0° in EtOH, which can also be obtained from Et *l*-(−)lactate.

d-(+)α-*Chloro*-N-p-*toluenesulphonylpropionamide*, m.p. 118°, $[\alpha]_{5467}$ +29·7° in EtOH, may be obtained from the *l*-(−)α-*p*-toluenesulphonoxy-compound and LiCl, or from Et d-(+)α-chloropropionate. l-(−)α-p-*Toluenesulphonoxy*-N-o-*carboxyphenylpropionamide*, m.p. 131°, $[\alpha]_{5893}$ −102·4° in EtOH, with LiCl affords d-(+)α-*chloro*-N-o-*carboxyphenylpropionamide*, m.p. 148°, $[\alpha]_{5893}$ +3·34° in $CHCl_3$ [also derived from *d*-(+)α-chloropropionyl chloride], and its Na salt with NaOEt and LiCl yields the *lactone* of α-*hydroxy*-N-o-*carboxyphenylpropionamide*, m.p. 236—238°, $[\alpha]_{5893}$ −449° in EtOH. Na *l*-(−)α-*p*-toluenesulphonoxy-*N*-*p*-carboxyphenylpropionamide on heating forms the "*lactone*" of α-*hydroxy*-N-p-*carboxyphenylpropionamide*, decomp. 270—290°, $[\alpha]_{5893}$ −161° in $C_5H_5N$, whilst the free amide with $NH_2Ph$ and LiCl gives d-(+)α-*chloro*-N-p-*carboxyphenylpropionamide*, m.p. 230—233°, $[\alpha]_{5893}$ +18·0° in EtOH. The replacement of the α-*p*-toluenesulphonoxy-groups in the neutral compounds by either OAc or OBz occurs with inversion. F. R. S.

**Fission of disulphides by alkali. II. Hydrolytic fission of the disulphide linking.** A. SCHÖBERL and H. ECK (Annalen, 1936, **522**, 97—115).—Partly a more detailed account of work previously reviewed (A., 1935, 1106). Alkaline hydrolysis of $(\cdot S\cdot CHR\cdot CO_2H)_2$ gives $SH\cdot CHR\cdot CO_2H$ (*A*) and $OH\cdot S\cdot CHR\cdot CO_2H$ (*B*); (*B*) then decompose to $H_2S$ and $COR\cdot CO_2H$ (*C*) [R may be H; when R is $CO_2H$ or $CH_2\cdot CO_2H$, the intermediate $CO(CO_2H)_2$ or $CO_2H\cdot CH_2\cdot CO\cdot CO_2H$ loses $CO_2$ to give $CHO\cdot CO_2H$ or $AcCO_2H$, respectively]. It is probable that (*B*) also undergo slight disproportionation to (*A*) and $SO_2H\cdot CHR\cdot CO_2H$. The formation of (*C*) is demonstrated by carrying out the hydrolysis with aq. NaOH in presence of $Pb(OAc)_2$ (to remove $H_2S$) and $p\text{-}NH_2\cdot NH\cdot C_6H_4\cdot CO_2H$ (I); acidification of the filtrate affords $p\text{-}CO_2H\cdot C_6H_4\cdot NH\cdot N{:}CR\cdot CO_2H$. Under these conditions αα′-disulphidobisphenylacetic acid (A., 1934, 1348) yields 25·6% of *phenylglyoxylic acid* p-*carboxyphenylhydrazone*, m.p. 217—219°; $[\cdot S\cdot CH(CO_2H)_2]_2$ and $(\cdot S\cdot CH_2\cdot CO_2H)_2$ afford 49·3 and 50%, respectively, of *glyoxylic acid* p-*carboxyphenylhydrazone*, decomp. > 265° [also obtained from $CHCl_2\cdot CO_2H$ and (I) in conc. aq. KOH], whilst $(\cdot S\cdot CHMe\cdot CO_2H)_2$ and αα′-disulphidodisuccinic acid (II) give 67·5 and 32%, respectively, of *pyruvic acid* p-*carboxyphenylhydrazone* (III), decomp. 236° (*Me*$_2$ ester, m.p. 166°, prepared with MeOH–HCl). A neutral solution of the Na salt of (II) is hydrolysed when boiled; in presence of (I), 1-phenyl-5-pyrazolone-3 : 4′-dicarboxylic acid (IV) [*Me*$_2$ ester, m.p. 242° (decomp.)] and some (III) are produced. (III) is also obtained from $CO_2H\cdot CO\cdot CH_2\cdot CO_2H$ and (I) in aq. NaOH; in neutral solution (III) and (IV) result, whilst in acid (IV) is the sole product. The *Me*$_2$ ester of 1-phenyl-5-pyrazolone-3 : 3′-dicarboxylic acid has m.p. 198° (decomp.).

Hydrolysis (aq. NaOH) of αα′-disulphidobis-β-phenylpropionic acid [formed by oxidation (5% $H_2O_2$, trace of $FeSO_4$) of $CH_2Ph\cdot CH(SH)\cdot CO_2H$ (Gränacher, A., 1922, i, 849) in neutral solution] gives α-thiolcinnamic acid, m.p. 129° (sinters at 125°) (lit. 119°) [oxidised (0·1*N*-I in EtOH or AcOH) to αα′-disulphidobiscinnamic acid, m.p. 179°], which may arise (partly) by loss of $H_2O$ from the intermediate $CH_2Ph\cdot CH(S\cdot OH)\cdot CO_2H$. H. B.

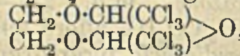
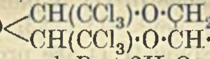
**Formation of hydrogen cyanide and formaldehyde by oxidation of organic substances.** R. FOSSE (Compt. rend., 1936, **202**, 445—448).—$CH_2O$ has been detected in the ammoniacal oxidation (electrolytic or $KMnO_4$) of glucose (I), sucrose, $(CH_2\cdot OH)_2$, glycerol (II), mannitol, $COMe_2$, AcOH, and glycine, which also form $CO(NH_2)_2$, HCNO, and HCN. In the cases of (I) and (II), $CH_2O$ is shown to be an intermediate in the formation of HCNO and $CO(NH_2)_2$. It is suggested that respiratory oxidation *in vivo* produces, in addition to energy, highly active intermediates for the synthesis of org. matter. Oxidation of $CH_2O$ by Parrod's method (A., 1935, 1109) yields no HCN. H. G. M.

**Colorimetric determination of acetaldehyde. III.** S. HÄHNEL (Svensk Kem. Tidskr., 1936, **48**, 61—64).—Modifications of the author's method (B., 1933, 328; this vol., 191) are described.

M. H. M. A.

**Effect of the reaction products on the thermal decomposition of gaseous acetaldehyde.** M.

LETORT (Compt. rend., 1936, **202**, 491—494; cf. A., 1934, 1073).—The decomp. of MeCHO is retarded by the products of reaction ($CO+CH_4$) (cf. A., 1926, 804; 1936, 191). An expression is developed which shows how, for the decomp. of pure MeCHO, the retardation due to the products changes the order of the reaction from 1·5 at the beginning to 1·8 during the course of the reaction. The mean observed val. for the latter is 1·87. H. G. M.

**Condensation of chloral and bromal with polyhydric alcohols.** A. N. MELDRUM and G. M. VAD (J. Indian Chem. Soc., 1936, **13**, 118—122).—*s*-Di-(βββ-trichloro-α-hydroxyethoxy)ethane (I) (de Forcrand, A., 1889, 689) (*diacetate*, b.p. 132—134°/15 mm., formed using $Ac_2O$ at room temp.) with $Ac_2O$–conc. $H_2SO_4$ or boiling AcCl gives the *anhydro*-derivative,  $\begin{matrix}CH_2{\cdot}O{\cdot}CH(CCl_3)\\ CH_2{\cdot}O{\cdot}CH(CCl_3)\end{matrix}\!\!>\!O$, m.p. 144°, which is stable to hot conc. $HNO_3$, boiling alkali, and conc. aq. $NH_3$ at 110°. Distillation of (I) under atm. pressure affords *glycol* βββ-*trichloroethylidene ether* [2-*trichloromethyl*-1 : 3-*dioxolan*], b.p. 200°, m.p. 42°, reduced (Zn dust, AcOH) to the ββ-*dichloroethylidene ether*, b.p. 118°/25 mm. Glycerol, chloral, and $H_2SO_4$ give γ-*hydroxy*-αβ-*di*-(β′β′β′-*trichloro*-α′-*hydroxyethoxy*)*propane* (II), b.p. 145—150°/15 mm., oxidised (conc. $HNO_3$ at 0°) to the *acid*,  $O\!<\!\begin{matrix}CH(CCl_3){\cdot}O{\cdot}CH_2\\ CH(CCl_3){\cdot}O{\cdot}CH{\cdot}CO_2H\end{matrix}$, m.p. 192—193° (*Na*+$2{\cdot}5H_2O$, and *Ba*+$2H_2O$, salts). Distillation of (II) under 70 mm. pressure affords glycerol αβ-β′β′β′-trichloroethylidene ether [4-hydroxymethyl-2-trichloromethyl-1 : 3-dioxolan], b.p. 162—164°/25 mm. (cf. Yoder, A., 1923, i, 309) (*acetate*, b.p. 205°/120 mm.; *nitrate*, m.p. 64°; *Me ether*, b.p. 140—142°/15 mm.; corresponding *chloride*, b.p. 130°/15 mm.), which is reduced to *glycerol* αβ-β′β′-*dichloroethylidene ether*, b.p. 160°/20 mm. (*acetate*, b.p. 188°/30 mm.). *Erythritol* αβ-*di*-(β′β′β′-*trichloro*-α′-*hydroxyethyl*) *ether*, m.p. 167—171° (*tetra-acetate*, m.p. 164°), is formed from erythritol and chloral at 100°. $(CH_2{\cdot}OH)_2$ and $CBr_3{\cdot}CH(OH)_2$ (III) at 130—140° give *s*-*di*-(βββ-*tribromo*-α-*hydroxyethoxy*)*ethane*, b.p. 145—147°/25 mm. (*diacetate*, b.p. 196°/135 mm.), which when distilled passes into *glycol* βββ-*tribromoethylidene ether*, m.p. 103—104°, also formed from $(CH_2{\cdot}OH)_2$, (III), and conc. $H_2SO_4$. Glycerol and (III) similarly yield γ-*hydroxy*-αβ-*di*-(β′β′β′-*tribromo*-α′-*hydroxyethoxy*)*propane* (IV), b.p. 205°/25 mm. (*triacetate*, b.p. 190°/155 mm.); in presence of conc. $H_2SO_4$, *glycerol* αβγ-*tri*-(β′β′β′-*tribromo*-α′-*hydroxyethyl*) *ether* (V) results. Distillation of (IV) and (V) under reduced pressure affords *glycerol* αβ-β′β′β′-*tribromoethylidene ether*, b.p. 210°/60 mm., and its γ-β′β′β′-*tribromo*-α′-*hydroxyethyl ether*, b.p. 145°/20 mm., respectively. H. B.

***iso*Propylideneglyceraldehyde. III. Synthesis of *d*-fructose and *d*-sorbose from *d*-glyceraldehyde or *d*-glyceraldehyde and dihydroxyacetone.** H. O. L. FISCHER and E. BAER (Helv. Chim. Acta, 1936, **19**, 519—532; cf. A., 1934, 635).—*d*-$OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CHO$ (I) (prep. from di*iso*propylidenemannitol improved to give a 86·2% yield) and 0·01*N*-$Ba(OH)_2$ give 95% of a 1 : 1-mixture of *d*-fructose (II) and *d*-sorbose (III), determined as phenylosazones; (II) is isolated free as Ca salt in good yield, the mother-liquor giving (III) after removal of the residual (II) by fermentation. The reaction is shown polarimetrically to be complete in 2 hr. (I), $CO(CH_2{\cdot}OH)_2$ (IV), and $Ba(OH)_2$, however, give a similar mixture in 40 min. Reaction thus proceeds by slow change of (I) to (IV), followed by a faster condensation of the enolic form of (I) with (IV). The above reaction and the fact that *iso*propylideneglyceraldehyde gives a branched-chain product show that condensation occurs only with $OH{\cdot}CH_2{\cdot}COR$. Absence of *d*-psicose and *d*-tagatose from the products shows preferential formation of products with opposite configurations at C3 and C4.

[With H. POLLOK.] A similar reaction occurs with $CH_2O$ and $CH_2Ac{\cdot}OH$, giving a 25% yield of $COMe{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, m.p. 37—38° (also obtained from $COMe{\cdot}CH{:}CH_2$ and $KMnO_4$ or $KClO_3$–$OsO_4$), which in turn with $CH_2O$ gives a $C_5$-sugar. R. S. C.

**Electrolytic reduction of organic compounds at the dropping mercury electrode. I.** A. WINKEL and G. PROSKE (Ber., 1936, **69**, [*B*], 693—706).—Under the experimental conditions introduction of Me into $CH_2O$ diminishes the reducibility, the effect being enhanced when a second Me becomes attached to CO, but not when Me is replaced by Et. Introduction of further Me groups into $COMe_2$ does not alter its behaviour; *cyclo*-hexanone and -pentanone resemble aliphatic ketones. Ph behaves oppositely to Me. With aromatic ketones the polarographic stages are very distinct, so that the method is peculiarly adapted to the aromatic series. When in the α-position to CO the effect of Ph is lost; it therefore depends on the presence of a conjugated system. Condensed ring residues are more effective than is Ph. The reduction potential is markedly affected by halogen, notably by I, and a second halogen enhances the effect of the first. OH attached to CO inhibits its reduction. The reduction potential is displaced towards the positive in sequence of decreasing effect by $C_2H_4I$, $C_2H_4Br$, $C_2H_4Cl$, 1-$C_{10}H_7$, Ph, and towards the negative by OH and Me. The influence of the several groups can be qualitatively evaluated by addition or subtraction of the vals. for the individual groups, but a quant. measurement is not yet possible, since the displacement of the potential depends on its abs. val. H. W.

**Conditions of condensation of acetone molecules with each other.** P. P. SURMIN (J. Gen. Chem. Russ., 1935, **5**, 1639—1641).—Condensation of $COMe_2$ proceeds most energetically in alkaline media, alcoholic alkalis being more efficacious than aq. The greatest yields of condensation products are obtained in presence of $CaC_2$ at the b.p.; the relative yields of products of higher b.p. rise with increasing amount of $CaC_2$. R. T.

**Semicarbazones of [dialkyl] ketones.** H. S. RHINESMITH (J. Amer. Chem. Soc., 1936, **58**. 596—597).—$CHEt(CO_2Et)_2$, $COMe{\cdot}CH{:}CH_2$, and EtOH–NaOEt (trace) give *Et heptan*-β-*one*-εε-*dicarboxylate*, b.p. 136—138°/2 mm. (*semicarbazone*, m.p. 116·5—117·5°), hydrolysed (cold dil. EtOH–KOH) to the *Et H* ester, b.p. 71—73°/2 mm. (*semicarbazone*, m.p. 114—115°), and thence (conc. EtOH–KOH) to the free acid, decarboxylated at 130° to *heptan-β-one-ε-carboxylic acid*, b.p. 135—137°/2 mm. [*semicarbazone*, m.p. 127—129°; *Me* ester, b.p. 75°/2 mm. (*semicarbazone*, m.p. 108°)]. $CHEt_2{\cdot}CH_2Br$, b.p. 144—145° (from the alcohol and $PBr_3$), with NaCN in 50% EtOH affords $CHEt_2{\cdot}CH_2{\cdot}CN$, b.p. 164—166°, which with MgEtBr yields *ε-ethylheptan-γ-one*, b.p. 171—173°/760 mm. (*semicarbazone*, m.p. 133—134°). Oxidation ($CrO_3$) of the carbinol from $Bu^{\beta}CHO$ and MgEtBr gives *ε-methylhexan-γ-one*, b.p. 135—137°/760 mm. (*semicarbazone*, m.p. 149—150°). The *semicarbazones* of γ-, b.p. 136—139°/760 mm., and δ-, b.p. 137—139°/760 mm., -methylhexan-β-one have m.p. 69—70° and 127—128°, respectively; that of ε-methylhexan-β-one, b.p. 143—144°/760 mm., has m.p. 146—147° (lit. 141°). The Grignard reagent from $CHMeEt{\cdot}CH_2I$, b.p. 137—140° (alcohol from *sec.*-BuMgI and $CH_2O$) and PrCHO give a carbinol, b.p. 157—163°, oxidised ($CrO_3$) to ζ-methyloctan-δ-one (*semicarbazone*, m.p. 75°). H. B.

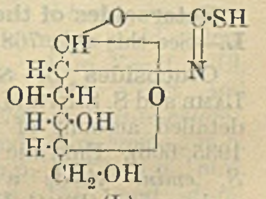
**Colour reaction of hexoses and their polymerides, and its application to colorimetric determination of glucose in blood.** J. A. SANCHEZ [with R. C. D'ALLESSIO] (J. Pharm. Chim., 1936, [viii], 13, 377—387).—Hexoses and polysaccharides derived from them, but not pentoses, give a rose-red coloration, the intensity of which is ∝ hexose concn., when their dil. (*e.g.*, 1 : 5,000) aq. solution is treated with warm conc. $H_2SO_4$. The absorption spectrum contains three bands (except in the case of galactose) with max. at 5300, 4920, and 5520 A. For the detection or determination of glucose (I), total blood or blood-serum is deproteinised with $CCl_3{\cdot}CO_2H$, and the colour produced by the above reaction is matched against that given by similarly treated blood-serum, freed from (I) by allowing glycolysis to proceed to completion at 37°, to which known amounts of (I) are added. The method is suitable for solutions with $<0{\cdot}1\%$ of (I). J. S. A.

**Cupro-alkali metal carbonate solution in the determination of reducing sugars. II. Modification of Pellet's solution.** C. Y. CHANG and H. A. SCHUETTE (Trans. Wis. Acad. Sci., 1935, 29, 381—388; cf. A., 1931, 199).—Pellet's $CuSO_4$–$NH_4Cl$–Na K tartrate–$Na_2CO_3$ solution (A., 1875, 666; 1878, 612) slowly and irreversibly deposits a ppt. and loses in reducing power (17·3% in 515 hr.). Mixture of $CuSO_4$–$NH_4Cl$ and tartrate–$Na_2CO_3$ solutions in the proportions of Pellet's solution immediately prior to the test leads to erratic results. More reproducible results and stable solutions are obtained by increasing the alkalinity, max. reducing power being found with 4·5*N*-$Na_2CO_3$; reaction is then complete in 40 min. at 90°. The reagents recommended are: (*A*) $CuSO_4,5H_2O$ 343·5 and $NH_4Cl$ 34·35 g. per litre; (*B*) Na K tartrate 216·52 and $Na_2CO_3$ 283·5 g. per litre. Solutions (*A*) and (*B*) are mixed in the proportions 1 : 4 just before use; 20 ml. of the mixed reagent and ≯ 0·1 g. of glucose or fructose or 0·22 g. of lactose or maltose in a total vol. of 80 ml. are heated in a stoppered flask at 90° for 45 min. Cu equivs. of the above-mentioned sugars are given; they are higher than for Pellet's solution, thus giving increased accuracy. This technique requires no blank determination, gives zero results for sucrose, and is accurate for mixtures of all the sugars named except for that of lactose with much sucrose. The reason for this exception is unknown. R. S. C.

**Benedict's qualitative [sugar] test.** J. FINE (Brit. Med. J., 1935, I, 1169—1170).—The test is adapted to the quant. examination of glucose. CH. ABS. (*p*)

**Synthesis of 5 : 6-benzhydrylidene-1 : 2-*iso*propylidene-*α*-*d*-glucofuranose. Catalytic hydrogenation of acetals of aromatic ketones and sugars.** P. E. PAPADAKIS (J. Amer. Chem. Soc., 1936, 58, 665—666).—1 : 2-*iso*Propylideneglucose (I) and $CPh_2Cl_2$ in $C_5H_5N$ at 0° give 5 : 6-*benzhydrylidene-1 : 2-*iso*propylideneglucose*, m.p. 147—148°, $[\alpha]_D^{22}$ +21·7° in $C_5H_5N$, which does not react with $CPh_3Cl$ and is reduced ($H_2$, Pd, MeOH–AcOH) to (I) and $CH_2Ph_2$. $CPh_2(OMe)_2$ (from $CPh_2Cl_2$ and MeOH in $C_5H_5N$) is similarly reduced to $CH_2Ph_2$. H. B.

**Behaviour of glucose towards thiocyanic acid.** G. ZEMPLÉN, Á. GERECS, and M. RADOS (Ber., 1936, 69, [*B*], 748—754).—Treatment of glucose and KCNS in $H_2O$ with 12*N*-HCl at room temp. slowly affords *μ-thiolglucoxazoline* (I), m.p. 172°, $[\alpha]_D^{20}$ +34·12° in $H_2O$. It does not reduce Fehling's solution. It does not behave towards alkali as a lactone, but its optical behaviour when treated with increasing quantities of NaOH indicates salt formation (I) with or without enolisation. N is partly evolved as $NH_3$ when it is boiled with alkalis. $Hg(OAc)_2$ gives cryst. additive compounds with varying Hg content. S is removed with difficulty by metallic salts, readily by oxidising agents. Reducing agents cause production of COS or $H_2S$, but do not give homogeneous products. With $NHPh{\cdot}NH_2$ (I) affords glucosephenylosazone in good yield. It is very sensitive towards hot 10% HCl; reducing substances are formed, but the reducing power remains < that calc. for glucose. (I) with anhyd. NaOAc and $Ac_2O$ at 100° gives the corresponding *tetra-acetate* (II), m.p. 120°, $[\alpha]_D^{23}$ +123·9° in $CHCl_3$, hydrolysed by NaOMe in $CHCl_3$ to (I) and unchanged by boiling EtOH or $NH_3$–MeOH at 0°. Partial hydrolysis of (II) by NaOMe–$CHCl_3$ yields the *triacetate*, m.p. 131·9°, $[\alpha]_D^{20}$ +107° in $CHCl_3$, re-acetylated to (II). (I), NaOH, and $H_2O_2$ give *μ-hydroxyglucoxazoline*, $[\alpha]_D^{20}$ +6·79° in $H_2O$, which reduces Fehling's solution to an extent depending on the duration of heating, is sensitive to boiling acids, loses part of its N as $NH_3$ when boiled with alkalis, and affords a yellow oil when treated with $NHPh{\cdot}NH_2$. Its *triacetate*, m.p. 139°, $[\alpha]_D^{17}$ +58·86° in $CHCl_3$, is obtained by the action of $H_2S$ in EtOH–AcOH on the *Hg* derivative $C_{28}H_{32}O_{18}N_2Hg$, m.p. 245° (decomp.), prepared from (II) and HgO in BuOH, and is converted by NaOAc and $Ac_2O$ at 100° into the *tetra-acetate*, m.p. 95°, $[\alpha]_D^{17}$ +104·8° in $CHCl_3$. H. W.



(I.)

**Nature of sucrose caramel.** G. VON ELBE (J. Amer. Chem. Soc., 1936, 58, 600—601; cf. Cunningham and Dorée, J.C.S., 1917, 111, 589).—

Caramel (I), prepared by heating sucrose (loss $\nless 12\%$) at atm. pressure or in a vac., is a colloidal dispersion of a lyophobic, humic substance (II) in a mixture of two protective substances (III), decomp. > 95°, $[\alpha]_{D}^{25}$ +24·5°, and (IV), decomp. > 140°, $[\alpha]_{D}^{25}$ +63°. Extraction of (I) with successive quantities of MeOH followed by $H_2O$ removes most of (III) and (IV); the residual (II) coagulates irreversibly to a dark brown, insol., and infusible mass showing a diffuse *X*-ray pattern. (III) and (IV) are separated by repeated pptn. of (IV) from MeOH with PrOH; they are thermally unstable, hygroscopic, amorphous powders which yield *acetates*. (III) and $NHPh{\cdot}NH_2$ give glucosazone and an oily product; (IV) affords similar products only after hydrolysis. (III) and (IV) show marked thermal stability and resistance to dissolution in presence of (II). H. B.

**Action of pyridine on maltose.** R. Sutra (Bull. Soc. chim., 1936, [v], 3, 145).—Maltose (I) when crystallised from $C_5H_5N$ gives the *compound*, $C_{12}H_{22}O_{11},2C_5H_5N$, m.p. 106°, stable at room temp., but decomposed by EtOH, regenerating (I). H. G. M.

**Heterosides of the fruits of *Sophora japonica*, L.**—See this vol., 768.

**Glucosides of *Strophanthus emini*.** I. D. Lamb and S. Smith (J.C.S., 1936, 442—447).—A more detailed account of work previously reported (B., 1935, 606). Enzymic hydrolysis of strophanthin from *S. emini* yields a new cardio-tonic monoside, *emicymarin* (I), $C_{30}H_{46}O_9$, sinters 160°, m.p. 207° (indefinite), $[\alpha]_{5461}^{20}$ +15·8°, $[\alpha]_{D}^{20}$ +12·8° in EtOH {*tetrahydrate*; *Ac*$_2$ derivative, m.p. about 278°, $[\alpha]_{5461}^{20}$ +27·8°, $[\alpha]_{D}^{20}$ +22·8° in MeOH; *H*$_2$-derivative, m.p. 151° (indefinite after sintering), $[\alpha]_{5461}^{19}$ +11·2°, $[\alpha]_{D}^{19}$ + 8·6° in EtOH, iso-*compound*, m.p. about 270° (previous sintering), $[\alpha]_{5461}^{25}$ +30·9°, $[\alpha]_{D}^{20}$ +26·2° in $C_5H_5N$, identical with trianhydroperiplogenin (Jacobs *et al.*, A., 1933, 1038)}, *anhydroemicymarigenin*, $C_{23}H_{32}O_4$, m.p. 269—277°, $[\alpha]_{5461}^{24}$ +67°, $[\alpha]_{D}^{24}$ +59° in $C_5H_5N$, and digitalose, m.p. 106° (after sintering; m.p. rises on keeping), converted by Br into digitalonolactone, m.p. 137—138°. (I) is an unsaturated $\Delta^{\beta\gamma}$-lactone; by enzymic hydrolysis it gives a monoside, allo-*emicymarin*, m.p. 248° (sinters 240°), $[\alpha]_{5461}^{23}$ +29·7°, $[\alpha]_{D}^{23}$ +24·6° in 95% EtOH, identical with the monoside obtained by Jacobs *et al.* (A., 1933, 278) direct from the seeds. F. R. G.

**Constituents of *Epimedium macranthum*, Morr and Decne. I. Chemical constitution of a new flavone glucoside of *E. macranthum*. 1.** S. Akai (J. Pharm. Soc. Japan, 1935, 55, 537—599).—Extraction of the dry leaves and roots with MeOH affords *icariin* (I), $C_{32}H_{39}O_{15}{\cdot}OMe$, m.p. 231—235°, $[\alpha]_{D}^{15}$ −87·09° in $C_5H_5N$ (*Ac*$_9$ derivative, m.p. 120°), which is hydrolysed (dil. $H_2SO_4$) to *icariside* I (II), $C_{26}H_{29}O_{11}{\cdot}OMe$, m.p. 256°, $[\alpha]_{D}^{15}$ −28·39° in $C_5H_5N$ (*Ac*$_7$ derivative, m.p. 143°; *Bz*$_7$ derivative, m.p. 151·5°), and rhamnose. Under other conditions (I) is hydrolysed to (II) and *anhydroicaritin* (III), $C_{21}H_{17}O_3(OH)_3$, m.p. 242—243° (*Ac*$_3$ derivative, m.p. 185°; *Bz*$_3$ derivative, m.p. 190·5°; *dimethylate*, m.p. 176°; *trimethylate*, m.p. 146—147°; *dihydrotrimethyl ether*, m.p. 134°; *dibromotrimethyl ether*, m.p. 189°; *Me*$_3$ *ether hydrochloride*, m.p. 162°). Hydrolysis of (II) with 50% $H_2SO_4$ yields β-*anhydroicaritin* (IV), $C_{20}H_{17}O_5{\cdot}OMe$, m.p. 222—223° (*Ac*$_2$ derivative, m.p. 228°; *Bz*$_2$ derivative, m.p. 299°; *Me*$_1$ *ether*, m.p. 191°; *Me*$_2$ *ether*, m.p. 221—222°), and glucose (V). Demethylation of (IV) gives 4′-*demethyl*-β-*anhydroicaritin*, $C_{20}H_{18}O_6$, m.p. 308—309° (*Ac*$_3$ derivative, m.p. 208°). (II) and (IV), with alkali at 250—260°, yield phloroglucinol (VI) and $p\text{-}OH{\cdot}C_6H_4{\cdot}CO_2H$. With 35% KOH in the presence of $H_2$, (II) yields (III) and *icaritin* (VII), $C_{21}H_{22}O_7$, m.p. 239—239·5° (*Ac*$_3$ derivative, m.p. 212°; *Ac*$_4$ derivative, m.p. 146·5°; *Bz*$_4$ derivative, m.p. 184°; *Me*$_2$ *ether*, m.p. 168·5°; *Me*$_3$ *ether*, m.p. 174°, and its *phenylurethane*, m.p. 213—214°), which with dil. $H_2SO_4$ affords (IV). The *Me*$_2$ *ether* of (III) with 10% EtOH–KOH yields anisic acid (VIII) and *icaritol* II, $C_{13}H_{14}O_3(OMe)_2$, m.p. 106° (*oxime*, m.p. 162—163°; *Me ether*, m.p. 99°), which, with KOH at 250—260°, yields (VI) and $Bu^{\beta}CO_2H$. The *Me*$_3$ *ether* of (III) similarly affords (VIII) and *icaritol* I (IX), $C_{13}H_{13}O_2(OMe)_3$, m.p. 128° (*oxime*, m.p. 115°; *oxime* of *Me* derivative, m.p. 139°; *Br*$_2$-derivative, m.p. 154°; *hydrochloride*, m.p. 106°), hydrogenated to *dihydroicaritol* I, m.p. 118—118·5°. Oxidation ($CrO_3$) of the Me ether of (VII) gives $COMe_2$ (?) and an aldehyde. With $H_2SO_4$, (IX) is cyclised to β-*icaritol* I, $C_{13}H_{13}O_2{\cdot}OMe$, m.p. 82° (*oxime*, m.p. 165°). On hydrolysis with emulsin, (I) yields *icariside* II (X), $C_{27}H_{30}O_{10}$, m.p. 204—205°, $[\alpha]_{D}^{15}$ −128·03° in EtOH (*Ac*$_5$ derivative, m.p. 88°; *Bz*$_5$ derivative, m.p. 225°), and β-glucose. (X), with dil. $H_2SO_4$, yields (III) and rhamnose, and, with 35% KOH, (III) and (VIII). (II) is hydrolysed by emulsin to (III) and (V). The *Me* derivative of (X) is hydrolysed (dil. $H_2SO_4$) to *anhydroicaritin* 7-*Me ether*, m.p. 204°, further methylated to *anhydroicaritin* 3 : 7-*Me*$_2$ *ether*, m.p. 174°. Ch. Abs. (*r*)

**Highly polymerised compounds. CXXXVI. Structure of starch. CXXXVII. Macromolecular structure of lichenin.** H. Staudinger and H. Eilers (Ber., 1936, 69, [*B*], 819—848, 848—851).—CXXXVI. Enzymic degradation of potato starch gives products of mol. wt. 10,000—20,000, which are very difficult to purify and free from ash. Controlled degradation with 2*N*-HCl or $HCO_2H$ gives more amenable materials of mol. wt. 10,000—100,000, which can be fractionated by pptn. from $H_2O$ by MeOH. The viscosity of these products has been measured in $H_2O$, $HCO{\cdot}NH_2$, *N*-NaOH, and $HCO_2H$ under varied conditions of temp. and concn. It is thus shown that the particles consist of macromols., and not micelles; the conclusion is strengthened by the conversion of degraded starches into their acetates, from which they are regenerated unchanged by cautious hydrolysis in absence of air. Nitrating acid causes degradation of the starch mol. which precedes esterification, since the nitrates are relatively stable in the mixture of acids. The form of the extended starch mol. differs greatly from that of the cellulose mol. $K_m$ of starch is 8—10 times < that of cellulose, so that a starch mol. equal in length to a cellulose mol. has about 8—10 times its wt. and contains 8—10 times as many glucose residues. A zigzag or meander form of the starch mol. is suggested which harmonises with its greater solubility. According to physical properties, starches of mol. wt. 10,000—100,000 are hemicolloidal in character, whereas according to particle wt. they belong to the mesocolloids. For this reason they have been frequently regarded as relatively simple, whereas they are of high mol. wt.

CXXXVII. The vals. $\eta_{sp}/C_{gm.}$ are const. for solutions of lichenin (I) in Schweitzer's reagent and $N$-NaOH provided the viscosity is low and $n_{sp}$ is the same for solutions of equal concn. in either solvent within the experimental limits. A macromol. structure of the colloidal particles of (I) is thus indicated; probably this is branched or bent. Treatment of (I) with nitrating acid caused degradation which precedes esterification. H. W.

**α-Amino-βγ-dihydroxy-*n*-butyric acid. III.** H. O. L. Fischer and L. Feldmann (Helv. Chim. Acta, 1936, **19**, 532—537; cf. A., 1932, 936).—*d-iso*-Propylideneglyceraldehyde (prep. without isolation from di*iso*propylidenemannitol) in MeOH with $NH_3$, followed by HCl, gives a 30% yield of *α-amino-βγ-dihydroxy*-n-*butyric acid*, decomp. 215° (discoloration from about 190°), $[\alpha]_D^{20}$ −13·73° in $H_2O$ [*Cu* salt; *phenylcarbamide*, $+H_2O$, m.p. 165° (decomp.), $[\alpha]_D^{17}$ +29·8° as Na salt in $H_2O$, and 2-$C_{10}H_7\cdot SO_2$ *derivative*, m.p. 180—181° (decomp. from 178—179°), $[\alpha]_D^{25-27}$ +12·5—13·45° as Na salt in $H_2O$], in which the configuration of the $>CH\cdot OH$ is fixed. The Strecker synthesis proceeds better with the *iso*propylidene than with the OH-compound. R. S. C.

**Synthesis of a αα′-diamino-ββ′-dihydroxyadipic acid.** H. O. L. Fischer and L. Feldmann (Helv. Chim. Acta, 1936, **19**, 538—543).—*iso*Propylidene-*d*-tartardialdehyde gives, by the Strecker synthesis, *αα′-diamino-ββ′-dihydroxyadipic acid*, m.p. 255—256° (decomp. from about 235°), $[\alpha]_D^{23-25}$ −24·1° to −25·09° in HCl [*Cu* salt, $+H_2O$; *diphenylcarbamide derivative*, m.p. 181—183° (decomp. from about 170°), $[\alpha]_D^{17}$ +26·9±2° in dry EtOH], in which the configuration of both $>CH\cdot OH$ is known. The acid gives a deep blue colour with ninhydrin, but other reactions are negative; it is not deaminated by rat's liver or kidney. R. S. C.

**Form of polypeptide chains. I. *dl*-Alaninehexapeptide.** G. Boehm (Biochem. Z., 1936, **284**, 322—328).—Aq. sols of hexa-(*dl*-alanyl)-*dl*-alanine (Abderhalden, A., 1932, 503) exhibit strongly positive streaming double refraction, both in "streaky" solutions containing needle-shaped particles and in solutions containing only amicrons; this shows the presence of long anisotropic micelles, and indicates a long chain formation, and not a spherical structure for the free peptide in solution. F. O. H.

**Isolation of *dl*-arginine from kidney autolysate.**—See this vol., 749.

**Constitution of reduction product of chloralacetamide.** A. N. Meldrum and G. M. Vad (J. Indian Chem. Soc., 1936, **13**, 117—118).—In agreement with Yelburgi and Wheeler (A., 1934, 770), $CCl_3\cdot CH(OH)\cdot NHAc$ (I) is reduced to $CCl_2{:}CH\cdot NHAc$, since the latter with $Cl_2$ in $CHCl_3$ at $< 60°$ gives *acet-αβββ-tetrachloroethylamide*, m.p. 128° [also obtained from (I) and $PCl_5$], which with $NH_2Ph$ in $C_6H_6$ affords *acet-βββ-trichloro-α-anilinoethylamide*, m.p. 146°. H. B.

**Carbon suboxide and its reactions with amines.** E. A. Pauw (Rec. trav. chim., 1936, **55**, 216—226).—$C_3O_2$ [determined by adding a measured vol. of its solution in $Et_2O$ to excess of $CO_2$-free $H_2O$, and titrating $CH_2(CO_2H)_2$ by $CO_3''$-free alkali (phenolphthalein)] reacts in $Et_2O$ with amines NHRR′ to form malondiamides $CH_2(CO\cdot NRR')_2$, diamines yielding heterocyclic compounds. $NH_3$ and aliphatic primary amines have been used to give the diamides $CH_2(CO\cdot NHR)_2$, where R = H, Me, Et, $Pr^a$, $Bu^a$, $Bu^\beta$, $\cdot[CH_2]_4\cdot Me$, $\cdot[CH_2]_2\cdot Pr^\beta$, and $\cdot[CH_2]_6\cdot Me$, and to give *malon-diallylamide*, m.p. 149°, and *-dibenzylamide*, m.p. 141° [both also obtained from $CH_2(CO_2Et)_2$]. $NHMe_2$, $NHEt_2$, $NHPr^a{}_2$, $NHBu^a{}_2$, piperidine, and piperazine, do not give isolable products with $C_3O_3$. $NHBu^\beta{}_2$ and $NH(\cdot[CH_2]_2\cdot Pr^\beta)_2$ give, however, *malon-bis(di*isobu*tylamide)*, m.p. 276°, and *-bis(di*iso*amylamide)*, m.p. 289°. The appropriate diamines yield *malonpentamethylenediamide*, $CH_2[\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot]_2CH_2$, m.p. 221—222°, and its NN′-*dibenzyl*, m.p. 123—124°, and N-*benzhydryl*, m.p. 112—114°, analogues. Aromatic amines yield malondiamides, $CH_2(CO\cdot NH\cdot C_6H_4\cdot X)_2$, where X = H, *p*-Cl, *p*-Br, *p*-I, *o*-, *m*-, and *p*-Me, *p*-OMe, *p*-OEt, and *m*-$NO_2$, and *malon-di*-o-, m.p. 176°, and *-di*-m-*chloro*-, m.p. 164°, *-di*-o-, m.p. 175°, and *-di*-m-*bromo*-, m.p. 175°, and *-di*-m-*iodo-anilide*, m.p. 182°, *-di*-o-, m.p. 164°, and *-di*-m-*anisidide*, m.p. 151°, and *-di*-o-, m.p. 165°, and *-di*-m-*phenetidide*, m.p. 157°; all these are also prepared from $CH_2(CO_2Et)_2$. *Malon-di-o-iodo-anilide*, m.p. 177°, and -di-*N*-methylanilide are further prepared from $C_3O_2$, which does not, however, yield malondi-*p*-nitroanilide [prepared from $CH_2(CO_2Et)_2$]. *o*-$NO_2\cdot C_6H_4\cdot NH_2$ does not combine with $C_3O_2$ or with $CH_2(CO_2Et)_2$, nor does NHPhEt combine with $C_3O_2$. Malondi-*p*-phenetidide is nitrated to *malondi-2-nitro*-p-*phenetidide*, m.p. 165—166°, hydrolysed to 2-nitro-*p*-phenetidine. *l*-Bornylamine yields l-*malondibornylamide*, m.p. 187° (from $C_3O_2$), or 192° [from $CH_2(CO_2Et)_2$], $[\alpha]_D^{20}$ −46°. *l*-Menthylamine does not react with $CH_2(CO_2Et)_2$, but with $C_3O_2$ gives l-*malondimenthylamide*, m.p. 177°, $[\alpha]_D^{20}$ −87·3°. α- and β-$C_{10}H_7\cdot NH_2$ with $C_3O_2$ give the corresponding diamides. 2-Aminopyridine combines with 1 mol. only of $C_3O_2$ (to give a ketenium base?). 5- and 8-Aminoquinoline react with $C_3O_2$ to form *malon-di-5-*, m.p. 265—271°, and *-di-8-quinolylamide*, m.p. 200—204°. The following are obtained from the appropriate amino-esters and $C_3O_2$: *$Et_2$ malondiamidoacetate*, m.p. 107°, *$Et_2$ malondi-α-amido*iso*butyrate*, and the *$Et_2$* esters of *dl*-malondialanide, and malondisarcoside. $NH_2\cdot CH_2\cdot CO_2H$ and $NH_2\cdot CO_2Et$ do not react with $C_3O_2$. The relative ease of formation, qual. solubility, and taste of the above diamides are recorded. E. W. W.

**Reaction between organic sulphur compounds and hydrogen peroxide. III. Reaction mechanism. 1.** R. Kitamura (J. Pharm. Soc. Japan, 1935, **55**, 300—349).—In alkaline solution $H_2O_2$ oxidises $R\cdot CS\cdot NHR'$ to $R\cdot CO\cdot NHR'$; the reaction mechanism and factors influencing the course

of the reaction are discussed. In neutral or acid solution sulphinic acids, disulphides, etc. are formed.
Ch. Abs. (*r*)

**Structure and formulæ of Prussian-blues and related compounds.**—See this vol., 670.

**Boron hydrides. V. Ethyl- and *n*-propyl-diboranes. VI. Action of ammonia on methyldiboranes.** H. I. Schlesinger, L. Horvitz, and A. B. Burg (J. Amer. Chem. Soc., 1936, **58**, 407—409, 409—414; cf. A., 1935, 738).—V. The prep. of *mono-*, *di-*, b.p. 67·1°, *tri-*, and *tetra-ethyl-*, m.p. −56·3°, *mono-* and *di-propyl-diborane* is described. The compounds are analogous to the corresponding Me derivatives of $B_2H_6$.

VI. The prep. of $B_3MeN_3H_5$, m.p. −59°, b.p. 87°; $B_3Me_2N_3H_4$, m.p. −48°, b.p. 107°; and $B_3Me_3N_3H_3$, m.p. 31·5°, b.p. 129°, is described. V.p. and heats of vaporisation have been determined and Trouton's const. has been evaluated. $BMe_2{\cdot}NH_2$ appears to exist in several forms between −60° and room temp.
E. S. H.

**Alkaline-earth cacodylates. I.** R. Tiollais (Bull. Soc. chim., 1936, [v], **3**, 70—87).—Pure Ca (+9, and 1 $H_2O$, and anhyd.), Ba (+9, 3, and 1 $H_2O$), and Sr (+13, 3, and 1 $H_2O$) cacodylates are prepared from cacodylic acid and the appropriate hydroxide. The solubility curves show breaks corresponding with changes in the no. of mols. of $H_2O$ of crystallisation. The solubilities of the anhyd. and the fully hydrated salts in MeOH and 95% and 100% EtOH have been determined. Aq. solutions of the salts are decomposed by atm. $CO_2$, and with $H_2S$ give *compounds*, probably thiocacodylates.
H. G. M.

**Synthesis of dihalogeno-thallium organic compounds.** N. N. Melnikov and G. P. Gratscheva (J. Gen. Chem. Russ., 1935, **5**, 1786—1790).—Compounds of the type $TlRX_2$ are readily prepared by the general reactions: $TlR_2X$ (I)+$TlX_3$ (II) → $2TlRX_2$ (III); $2TlR_3$+(II) → 3(III). Different by-products, in amounts increasing with the at. wt. of X, are formed by the reactions: (I)+(II) → $Tl_2X_4$+2RX; (III) → RX+TlX; 2(III) → (I)+(II); $TlR_3$+(II) → (I)+RX+TlX; $2TlR_3$+(II) → 2(I)+TlX+$R_2$. The following *compounds* are described; $TlMeBr_2$, decomp. at 140—160°, $TlEtCl_2$, decomp. at 180°, $TlEtBr_2$, decomp. at 140—160° (1 : 1 *compound* with $C_5H_5N$), *iso*-$C_5H_{11}{\cdot}TlCl_2$, decomp. at 210°, *iso*-$C_5H_{11}{\cdot}TlBr_2$, decomp. at 95—110°, *p*-$C_6H_4Cl{\cdot}TlCl_2$,$TlPhCl_2$, decomp. at 240°.
R. T.

**Magnetochemical investigations of organic substances. VII. Pentaphenyl*cyclo*pentadienyl.** E. Müller and I. Müller-Rodloff (Ber., 1936, **69**, [*B*], 665—668; cf. A., 1935, 1453).—At room temp. the observed data for the solid material are in harmony with a completely monomeric radical and the Σ condition. Curie's law is not quite exactly obeyed, but the small divergencies do not indicate an appreciable course moment. At lower temp. the divergencies are less than those observed with tridiphenylmethyl, and are possibly due to changes in the cryst. condition or incipient association. All C and N radicals examined appear to exist almost exclusively in the Σ condition.
H. W.

**Catalytic dehydrogenation of *cyclo*hexane.** V. I. Karshev, M. G. Severjanova, and A. N. Sivova (J. Appl. Chem. Russ., 1936, **9**, 269—278).—The activity of a no. of catalysts in promoting dehydrogenation of *cyclo*hexane at 500—550°, with production of aromatic compounds, rises in the series $Al_2O_3$ < Cr–Cu–$H_3PO_4$–$Al_2O_3$ < $CrO_3$–$H_3PO_4$ < Cr–Cu.
R. T.

**Thermal decomposition of dimethyl*cyclo*hexanes.** J. A. Arbusov and B. M. Michailov (Compt. rend. Acad. Sci., U.R.S.S., 1935, **4**, 337—340; cf. A., 1935, 73).—The yields of butadiene (mol. % calc. on the hydrocarbon decomposed) obtained by heating 1 : 2- (I), 1 : 3- (II), and 1 : 4-dimethyl*cyclo*hexane (III) with $H_2O$ at 700—750° are, respectively, 20·7, 18·4, and 23·9. The other gaseous products [vol. % in parentheses for (I), (II), and (III), respectively] obtained (at 700°) are $H_2$ (18·4, 16·8, 17·0), saturated hydrocarbons (31·1, 32·0, 29·7), unsaturated hydrocarbons (50·0, 50·8, 52·6), acetylenic hydrocarbons (1·5, 1·3, 0·9), $C_3H_6$+$C_4H_8$ (14·4, 22·3, 24·1), and $C_2H_4$ (26·8, 19·1, 16·8).
J. W. B.

**Fluoro*cyclo*hexane.** F. Swarts (Bull. Acad. roy. Belg., 1936, [v], **22**, 105—121).—When *cyclo*hexyl bromide (I) is distilled (Pt vessels) at 130° (5—6 days) with $Hg_2F_2$, and finally at 140°/100 mm., a 30% yield of *cyclo*hexyl fluoride (II), b.p. 43·2°/100 mm., f.p. 13°, is obtained with unchanged (I), 31% of *cyclo*hexene (III) (removed by Br-addition at 0°), HF, HBr, and, by extraction of the residue with boiling $C_6H_6$, a *polymeride* $(C_6H_{10})_n$ of (III). When heated, especially in glass, (II) readily loses HF to give (III); conc. $H_2SO_4$, $Mg(ClO_4)_2$, $P_2O_5$, $CaCl_2$, and HF, but not Pt-black, catalyse this elimination. (II) is stable towards dil. NaOH and fused $K_2CO_3$, and is attacked only slowly by Na to give (III), *cyclo*hexane, and a trace of a liquid, b.p. 232—235°, probably a mixture of *cyclo*hexyl*cyclo*hexene and di*cyclo*hexyl. No appreciable formation of a Grignard compound occurs with (II)–Mg–$Et_2O$. With MgPhBr and MgEtBr the main reaction is removal of HF to form (III). With Br–AcOH (II) gives mainly 1 : 2-dibromo*cyclo*hexane [from the initial product, (III)] and only a trace of bromofluoro*cyclo*hexane, b.p. 80°/30 mm.; reaction is rapid in light and is catalysed by the liberated HBr. With fuming $HNO_3$ at −10° (II) gives adipic and a trace of picric acid.
J. W. B.

**Catalytic reduction of organic fluorine compounds. III. Reduction of *cyclo*hexyl fluoride.** F. Swarts (Bull. Acad. roy. Belg., 1936, [v], **22**, 122—124).—Contrary to the rapid hydrogenation of PhF with $H_2$–Pt-black, with elimination of HF, absorption of $H_2$ by *cyclo*hexyl fluoride is negligible under the same conditions. An electronic explanation, based on the symmetrical group $\cdot CH_2F$ in the latter and the unsymmetrical group $>CHF$ in the former, is outlined.
J. W. B.

**Autoxidation of cyclic ethylenic hydrocarbons. I.** R. Dupont (Bull. Soc. chim. Belg., 1936, **45**, 57—64).—Autoxidation of 1-methyl-$\Delta^1$-*cyclo*hexene yields 1-methyl-$\Delta^1$-*cyclo*hexen-6-one, methyl*cyclo*hexenol, and 1-methyl-*trans*-1 : 2-*cyclo*hexanediol, whilst 1-methyl-$\Delta^3$-*cyclo*hexene gives an unidentified peroxide, b.p. 67—70°, and 1-methyl-*trans*-3 : 4-*cyclo*hexanediol. The gaseous products contain approx. 50% of $H_2$ in each case. R. S.

**Processes of dehydration. IV. Dehydrogenation of *cyclo*heptane, *cyclo*octane, and methylated *cyclo*heptanes to aromatic hydrocarbons.** L. Ruzicka and C. F. Seidel (Helv. Chim. Acta, 1936, 19, 424—433).—*cyclo*-Heptane (I) and -octane (II) derivatives with Se give $C_6H_6$ derivatives under the conditions normally used for obtaining $C_{10}H_8$ derivatives from their $H_{10}$-derivatives. (I) is unchanged at 350—360°, but at 440° gives PhMe. Methyl*cyclo*heptane, unchanged at 410°, gives at 440° PhEt, *o*- and *p*-xylene. (II) at 390—410° gives *p*-xylene. 1 : 2 : 2-*Trimethyl*cyclo*heptane* (from the semicarbazone of the 3-ketone and Na–EtOH at 200—210°), b.p. 104—105°/100 mm., with Se at 420° (only slowly at 400°) gives *m*-$C_6H_4MePr$ and 1 : 2 : 3-$C_6H_3Me_3$ (III); with Pd at 420° it affords (III) and other products. 1 : 1 : 4-*Trimethyl*-$\Delta^1$-cyclo*heptene* (*eucarvene*) (IV) (from tetrahydrocarveol and $KHSO_4$ at 210°), b.p. 161—165°/720 mm., is almost unaffected by Se at 340°, but at 370° gives a hydrocarbon, oxidised to *m*-$C_6H_4(CO_2H)_2$, but 1 : 1 : 4-*trimethyl*-cyclo*heptane* (*eucarvane*) (from tetrahydroeucarvone-semicarbazone and Na–EtOH at 200—210°), b.p. 162—163°/720 mm., with Se at 390—400° gives *m*-$C_6H_4MeEt$ and (III). *cyclo*Pentadecane and Se at 390—410° give a mixture, which does not contain aromatic hydrocarbons. 1 : 1 : 3-*Trimethyl*-2-*butyl*-cyclo*hexane* (from tetrahydroionone semicarbazone), b.p. 94—95°/10 mm., is unaffected by Se at 350°, but at 390—400° affords *m*-xylene and 1 : 3 : 2-$C_6H_3Me_2Bu$. *trans*-Decalin and Se at 370—390° (not at 340—360°) or, better, Pd–C at 320—340° give $C_{10}H_8$. The structures of the products are proved by oxidation to acids and by-products may have been undetected. It is uncertain whether fission precedes dehydrogenation or vice versa and whether (IV) yields *m*-$C_6H_4MeEt$ or *m*-xylene [by way of (III)]. R. S. C.

**Fused carbon rings. VII. Preparation of cyclic hydrocarbons from unsaturated tertiary alcohols. Synthesis of *cis*-9-methyl-octalin and -decalin, and a proof of the presence of the angular methyl group.** D. C. Hibbit and R. P. Linstead (J.C.S., 1936, 470—476).—$CHR{:}CH\cdot[CH_2]_n\cdot CO_2Et$ (cf. A., 1931, 935; 1935, 195) with MgMeI gives $CHR{:}CH\cdot[CH_2]_n\cdot CMe_2\cdot OH$ (I) which with $H_3PO_4$ yields $CHR{:}CH\cdot[CH_2]_{n-1}\cdot CH{:}CMe_2$ when $n=1$, R=Et and when $n=2$, R=H or Me, but when $n=3$, R=H, yields 1 : 1-dimethyl-$\Delta^3$-*cyclo*hexene. The following new *pentenylcarbinols* (I) were prepared: *dimethyl*-$\Delta^4$-, b.p. 65—66°/15 mm. (*phenylurethane*, m.p. 67—68°), *dimethyl*-$\Delta^3$-, b.p. 70°/17 mm. (*phenylurethane*, m.p. 89°), *dimethyl*-$\Delta^2$-, b.p. 63—64°/20 mm., m.p. −27° to −28° (corr.). A method for the synthesis of 9-methyloctalin is deduced. The Na compound from Et *cyclo*hexanone-2-carboxylate in PhMe with $CH_2{:}CH\cdot CH_2\cdot CH_2Br$ yields *Et* 2-$\Delta^{\gamma}$-*butenyl*cyclo*hexanone-2-carboxylate*, b.p. 156—158°/25 mm., hydrolysed [$Ba(OH)_2$] to 2-$\Delta^{\gamma}$-*butenyl*cyclo*hexanone* (II), b.p. 112—114°/28 mm. (*semicarbazone*, m.p. 127°) and the acid (not purified) corresponding with *Et* 1-$\Delta^{\gamma}$-*butenylpimelate*, b.p. 161—162°/11 mm., converted (Dieckmann) into *Et* 2-$\Delta^{\gamma}$-*butenyl*cyclo*hexanone-6-carboxylate*, b.p. 146—148°/11 mm., hydrolysed [$Ba(OH)_2$] to 1-$\Delta^{\gamma}$-*butenylpimelic acid*, m.p. 39°, and (II), converted (Grignard) into 1-*methyl*-2-$\Delta^{\gamma}$-*butenyl*cyclo*hexanol*, b.p. 102—104°/13 mm., dehydrated ($H_3PO_4$) to cis-9-*methyl*-$\Delta^2$-*octalin* (III), b.p. 82°/14 mm., reduced ($H_2$–Pt) to cis-9-*methyldecalin*, b.p. 82°/11 mm., converted by $AlCl_3$ into *trans*-9-methyldecalin. The structure of (III) is proved by oxidation ($KMnO_4$) to trans-, m.p. 194—196°, and cis-1-*methyl*cyclo*hexane*-1 : 2-*diacetic acid*, m.p. 160—163°, both of which are converted [$Ba(OH)_2$] with loss of $CO_2$ into 9-*methyl-2-hydrindanone*, b.p. 109°/20 mm., 219°/760 mm., m.p. indefinite (glass) (trans- and cis-*semicarbazones*, m.p. 238° and 220°), oxidised ($HNO_3$) to trans-, m.p. 162—164°, and cis-1-*methyl*cyclo*hexane*-1 : 2-*dicarboxylic acid*, m.p. 175°. $n_D$, $d$, and $[R_L]_D$ are recorded for many of these compounds. F. R. G.

**Metallic titanium in organic synthesis.** V. N. Sharma and S. Dutt (J. Indian Chem. Soc., 1935, 12, 774—780).—Ti may be successfully used as the metallic reactant in Zincke's and Friedel and Crafts' reactions, but is unsatisfactory for Ullmann's reaction, reaction occurring only when the halogen is loosely bound in the org. mol. It is unsatisfactory as a neutral reducing agent. Several examples of each reaction are given. H. G. M.

**Influence of solvent on the course of chemical reactions. V. State of the benzene molecule in solution.** K. Lauer and R. Oda (Ber., 1936, 69, [*B*], 851—861; cf. this vol., 300).—Examination of the absorption spectrum of $C_6H_6$ in AcOH, *cyclo*hexane (I), *cyclo*hexene (II), and $C_2Me_4$ combined with Henri's earlier measurements shows that all bands of it are displaced towards longer λ in all the media used, that the permanent dipole of the solvent does not appear to be related to the displacement, and that the most marked total displacement occurs in $CCl_4$. The solvent appears to exercise three actions which result in band displacements of the solute; (*a*) impediment of the association of the dissolved mols. by formation of its proper, voluminous associates, (*b*) hindrance of association by its own mol. form, and (*c*) association of the solvent mols. with the solute mols. Saturated dipolar mols. such as $H_2O$, EtOH, and $Et_2O$ belong to the first group, saturated non-polar mols. such as hexane and (I) to the second group. All three actions are present simultaneously in AcOH. $C_2Me_4$, (II), and liquid $C_6H_6$ belong to group (*b*), whilst $CCl_4$ is the sole exclusive representative of group *c*. Determination of the rates of reaction of Br on $C_6H_6$, PhMe, and tetrahydronaphthalene in hexane shows that bromination occurs at associated and non-associated $C_6H_6$ mols. The apparent constancy of the heat of activation in very dil. solution is caused by the small heat of association. The rapid reaction after further dilution is due to increase in the no. of non-associated mols. recognised by the increasing action const. The reason of the increase of the action consts. in conc. solution is increase in the mol. size by association and the consequent increase of the sensitive region. The results of measurements in $H_2O$, AcOH, and $CCl_4$ are discussed. It is concluded that the displacements observed in the spectrum of non-polar mols. in various solvents is caused by the formation of organised mol. aggregates in which the individual mols. have an altered affinity field and changed region of susceptibility. All reactions hitherto investigated occur with associated and non-associated mols. Heats of dissolution, solvation, and association of the partners in the reaction are expressed in the criteria of the changes, so that addition occurs previously to substitution. H. W.

**Preparation of deuterobenzene.** A. Klit and A. Langseth (Z. physikal. Chem., 1936, 176, 65—80).—$C_6D_6$ containing up to 98% D has been prepared by exchange reaction between DCl and $C_6H_6$ catalysed by anhyd. $AlCl_3$. For pure $C_6D_6$ the vals. $d_4^{20}$ 0·9483 and m.p. 6·64° have been calc. The equilibrium const. of the simplified exchange reaction $CH+DCl \rightleftharpoons CD+HCl$ is $\sim 1{\cdot}6$. In a mixture of various deuterobenzenes not containing a catalyst there is no exchange of H atoms between the mols. When exchange occurs, the D atoms are distributed between the benzene nuclei in such a way that the product is a mixture of the possible isomeric deuterobenzenes in such proportions as correspond with the laws of probability. R. C.

**Reactions of hexadeuterobenzene.** H. Erlenmeyer, H. Lobeck, and A. Epprecht (Helv. Chim. Acta, 1936, 19, 546—547).—When $C_6D_6$, $ClCO{\cdot}NH_2$, and $AlCl_3$ react in $CS_2$ and the complex is decomposed with 99·6% $D_2O$, the amide (I) gives on hydrolysis $C_6D_{3{\cdot}09}H_{1{\cdot}91}{\cdot}CO_2H$, as when the complex is decomposed with $H_2O$ (this vol., 604), showing that exchange of D with the H of $ClCO{\cdot}NH_2$ occurs during condensation. (I) gives by the Hofmann reaction $C_6D_{3{\cdot}178}H_{1{\cdot}822}{\cdot}NHAc$, m.p. 114·3°, *i.e.*, without exchange of H and D. Reaction of $C_6D_6$ with PhNCO and $AlCl_3$ in $CS_2$, followed by decomp. with $D_2O$, gives nearly pure $C_6D_5{\cdot}CO{\cdot}NDPh$, which with molten KOH loses D to give $C_6D_{0{\cdot}81}H_{4{\cdot}19}{\cdot}CO_2H$. R. S. C.

**Additive products of halogens and benzene derivatives. IV. Addition of chlorine and bromine to monohalogenobenzenes.** T. van der Linden (Rec. trav. chim., 1936, 55, 282—292).—$Cl_2$ and PhF, exposed to light in a sealed tube, afford *chlorofluorobenzene hexachloride*, m.p. 213—215°, *fluorobenzene hexachloride*, b.p. 112—117·5°/0·5—0·6 mm., and a more highly chlorinated product. Similarly, $Cl_2$ and PhBr afford a chlorobromobenzene hexachloride, m.p. 254—256°, and unidentified products. $Cl_2$ and PhI give $C_6Cl_5I$, $p$-$C_6H_4ClI$, and probably 2 : 4 : 5-$C_6H_2Cl_3I$; no additive products were found. Br (6 atoms) and PhF react with evolution of HBr; after 7 months in sunlight in a sealed tube Br was still present. The crystals formed are probably *bromofluorobenzene hexabromide* (I), m.p. 161°; an *isomeride*, m.p. 252°, a *bromofluorobenzene*, and a *dibromofluorobenzene* are also obtained. Br (1 atom) and PhF in 20 days afford a mixture of $C_6H_4BrF$ isomerides, b.p. 154—158°, two *fluorobenzene hexabromides*, m.p. 127—129° and 154—156°, and (I). Br (1 atom) and PhCl afford $p$-$C_6H_4ClBr$ and *chlorobenzene hexabromide*, m.p. 126°. Br and PhBr give $p$-$C_6H_4Br_2$ and a *bromobenzene hexabromide*, m.p. 146°. Br and PhI afford I and $p$-$C_6H_4BrI$. P. G. C.

**Action of aromatic nitro-compounds on magnesium aryl halides.** D. N. Kirsanov and P. A. Solodkov (J. Gen. Chem. Russ., 1935, 5, 1487—1493).—The reaction consists of $RNO_2+MgXR'$ (I) $\rightarrow ONRR'{\cdot}OMgX$ (II); (I)+(II) $\rightarrow NRR'{\cdot}OMgX$ (III)$+R'O{\cdot}MgX$; (III)+2(I) $\rightarrow RR'+NRR'{\cdot}MgX+(MgX)_2O$. The final products have been isolated and identified in the cases $R=R'=Ph$, $X=Br$; $R=\alpha$-$C_{10}H_7$, $R'=Ph$, $X=Br$; $R=Ph$, $R'=\alpha$-$C_{10}H_7$, $X=Br$; $R=Ph$, $R'=p$-$C_6H_4Me$, $X=Br$. R. T.

**Attempted preparation of benzyl fluoride from phenyldiazomethane.** C. L. Tseng, (Miss) P. T. Chia, and T. S. Ho (Sci. Rep. Nat. Univ. Peking, 1936, 1, 9—16).—$CHPhN_2$ and 40% aq. $H_2F_2$ give $(CHPh{:})_2$ and a trace of PhCHO. R. S. C.

**Cracking process. Pyrolytic transformation of *p*-xylene and *m*-xylene.** G. Baddeley and J. Kenner (Ber., 1936, 69, [*B*], 902—904).—Analogy is traced between the actions of heat and $AlCl_3$ on hydrocarbons. Passage of $p$-xylene (I) vapour through a $SiO_2$ tube at 800° gives $C_6H_6$, PhMe, 2 : 6-dimethylanthracene (II), and a little $m$-xylene (III). Under similar conditions (III) is much more extensively carbonised; it gives $C_6H_6$, PhMe, $C_{10}H_8$, and anthracene, but apparently not (I) or (II). H. W.

**Chlorination and nitration by nitrosyl chloride.** R. Perrot (Compt. rend., 1936, 202, 494—495).—Addition of NOCl to phenylethylene derivatives in $CCl_4$ at room temp. is always accompanied by oxidation, which accounts for the small yields of the expected nitrosochloride. $N_2$, $NH_4Cl$, and sometimes $NH_2OH,HCl$ are also formed, together with an oil which loses HCl on distillation giving a mixture of nitrated and chlorinated products. Thus styrene yields $CHPhCl{\cdot}CH_2Cl$, $CHPh{:}CH{\cdot}NO_2$, and a compound, m.p. 118° (decomp.), which contains two N to one of Cl and behaves like a nitrosochloride, giving with $C_5H_{11}N$ a nitro-amine, m.p. 136°. α-Chlorostyrene is converted into its αββ-trichloro- and αβ-dichloro-β-nitro, b.p. 148—150°/20 mm., derivatives. $CPh_2{:}CH_2$ gives a mixture of $Cl_1$- and $(NO_2)_1$-derivatives, and some $CPh_2{:}CH{\cdot}NO_2$. $CPh_2{:}CHMe$ gives its β-Cl-derivative, m.p. 39°, and a compound, m.p. 103°, considered to be $CPh_2Cl{\cdot}CHMe{\cdot}NO_2$. $CPh_2{:}CMe_2$ reacts slightly with NOCl and $CPh_2{:}CPh_2$ not at all, except at about 150° with the formation of $CPh_2Cl_2$ and products containing nuclear Cl. Other styrene derivatives yield mixtures difficult to separate. *cyclo*Hexene gives a mixture of 1 : 2-dichloro- and chloronitroso-*cyclo*hexane. H. G. M.

***o*-Divinylbenzene and naphthalene.** K. Fries and H. Bestian [with, in part, W. Klauditz] (Ber., 1936, 69, [*B*], 715—722).—Spectrochemical evidence shows that in the formation of $C_{10}H_8$ from $o$-divinylbenzene (I) ring closure is not accompanied by "optical neutralisation of valencies," and does not therefore involve appreciable change in the state of union and the internal compensation of the conjugated system. The transition of $\Delta^{\alpha\gamma\epsilon}$-hexatriene into $C_6H_6$ and of phenylbutadiene into $C_{10}H_8$ is accompanied by marked change in optical properties and chemical behaviour. ββ′-*o*-Phenylenediacrylic acid (II) (*$Me_2$* ester, m.p. 68°, and its *tetrabromide*, m.p. 141°; *$Et_2$* ester, m.p. 81°, and its *tetrabromide*, m.p. 138°; *dichloride*, m.p. 84°; *dianilide*, m.p. 231°) evolves $CO_2$ when heated with production of a (?) polymeride of (I); its Na salt is transformed by distillation with soda–lime mainly into $C_{10}H_8$. Short treatment of (II) with boiling $Ac_2O$ leads to the mixed *anhydride*, $C_6H_4(CH{:}CH{\cdot}CO{\cdot}OAc)_2$, m.p. 94° (decomp.), which passes when heated at 120°/vac. into $Ac_2O$ and ββ′-*o-phenylenediacrylic anhydride*, m.p. 254—256° (decomp.), unusually stable towards alkali hydroxide. ββ′-*o*-Phenylenedipropionic acid, m.p. 171°, readily prepared by hydrogenating (II) under pressure at room temp. in presence of Ni, Co, or mixed Cu catalyst, is converted by the successive action of $SOCl_2$ and $NH_3$–$H_2O$ into ββ′-*o-phenylenedipropionamide*, m.p. 195°, transformed by KOH and Br into o-ββ′-*diaminoethylbenzene*, b.p. 130—131°/1 mm. [*hydrochloride*, m.p. 255—265° (decomp.); *$Ac_2$*, m.p. 111°, and *$Bz_2$*, m.p. 154°, derivatives], not identical with the product described by von Braun *et al.* (A., 1917, i, 130). The corresponding diquaternary *iodide*, $C_{16}H_{30}N_2I_2$, m.p. 310° (decomp.), is converted by treatment with $Ag_2O$ and distillation into (I), b.p. 73—74°/12 mm., which is stable in the dark, but rapidly polymerises in direct sunlight. Hydrogenation ($PtO_2$) of (I) affords o-*diethylbenzene*, b.p. 66—67°/12 mm., 176—177°/760 mm. Partial hydrogenation of (I) and treatment of the product with Br in $CHCl_3$ leads to unchanged (I), its tetrabromide, and, mainly, o-*ethyl-αβ-dibromoethylbenzene*, b.p. 141—142°/12 mm., which is debrominated by Mg in $Et_2O$ to o-*ethylvinylbenzene*, b.p. 68—68·5°/12 mm.

H. W.

**Plano-radiate compounds. III. Hexasulphones of hexamethylbenzene.** H. J. Backer (Rec. trav. chim., 1936, **55**, 17—21).—The following *compounds*, $C_6(CH_2{\cdot}SO_2{\cdot}R)_6$ are obtained by oxidation of the appropriate thio-ether with $H_2O_2$–AcOH: R=Me, m.p. > 360°; Et (+2AcOH), m.p. 340°; $Pr^{\alpha}$, m.p. 305°; $Pr^{\beta}$ (+2AcOH), m.p. 340°; $Bu^{\alpha}$, m.p. 315—316°; $Bu^{\beta}$, m.p. 289—290°; *sec.*-Bu (+AcOH), m.p. 260—261°; $Bu^{\gamma}$, m.p. > 360°; *n*-amyl, m.p. 279—281°; *tert.*-amyl (+2AcOH), m.p. > 360°; *n*-hexyl, m.p. 266—267°; Ph (+AcOH), m.p. 320—325°; *p*-$C_6H_4Me$, m.p. 282°; *p*-$C_6H_4Bu^{\gamma}$, m.p. 295—300°; and $CH_2Ph$, m.p. 334°. These compounds crystallise readily and are not very sol. $C_6(CH_2{\cdot}S{\cdot}C_6H_4Bu^{\gamma})_6$ crystallises with 1 mol. of heptane, 2 mols. of $C_6H_6$, and 2 mols. of *m*-xylene, respectively, from these solvents.

H. G. M.

**Dipole moment and molecular structure. XVI. Configuration of ethylenic compounds.** E. Bergmann (J.C.S., 1936, 402—411).—A vanishing dipole moment (μ) for *iso*stilbene (Wildschut, Diss., Delft, 1932), stilbene (Smyth *et al.*, A., 1931, 669), $(NO_2{\cdot}C_6H_4{\cdot}CH{:})_2$, m.p. 225°, $(CClPh{:})_2$, m.p. 144°, and $(C[NO_2]Ph{:})_2$, m.p. 186°, indicates a *trans* structure. The following finite vals. indicate a *cis* structure: $(CClPh{:})_2$, m.p. 60°, μ 2·69, [*compound* with $(CPh{:})_2$, m.p. 67—69°], $(CBrPh{:})_2$, m.p. 68°, μ 2·53 [*compound* with $(CPh{:})_2$], *p*-$C_6H_4Cl{\cdot}CPh{:}CBrPh$, m.p. 160°, μ 2·61, or m.p. 113°, μ 1·57, $CPh{:}CClPh$, μ 1·53. The following vals. of μ were also obtained: α-bromostilbene, m.p. 31°, 1·38 (liquid), 1·30, Et, 1·84, Et *allo*-, 1·77, Et β-phenyl-, 1·98, Me α-phenyl-cinnamate, 1·92; *o*-$C_6H_4Ph{\cdot}CN$, 3·81; Et *p*-nitro-, 3·50, and Me *p*-nitro-α-phenyl-cinnamate, 3·78, indicating *trans* structures; *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2Et$, 3·84; of Me, 1·89 Et, 1·98 (from acid m.p. 134°), and Me αβ-dibromocinnamate 2·68 (from acid, m.p. 100°) (the last is $\mathrm{{}^{Ph}_{Br}\!>\!C{:}C\!<\!{}^{CO_2H}_{Br}}$); of Et, 2·63 (from acid, m.p. 159°) and Me β-bromocinnamate, 1·81 (from acid, m.p. 134°) (the latter is $\mathrm{{}^{Ph}_{Br}\!>\!C{:}C\!<\!{}^{CO_2H}_{H}}$ contrary to Auwers *et al.*; A., 1932, 271); benzylidene-, 2·92, benzylidene-*p*-bromo-, 2·93, αβ-dibromobenzylidene- (m.p. 113—114°), 3·17 (hence $\mathrm{{}^{Ph}_{Br}\!>\!C{:}C\!<\!{}^{Br}_{COPh}}$), β-bromobenzylidene-, 3·59 (hence $\mathrm{{}^{Ph}_{Br}\!>\!C{:}C\!<\!{}^{H}_{COPh}}$), α-bromobenzylidene-, 3·87, *p*-bromobenzylidene-, 2·47 (hence *trans*), *pp*′-dibromobenzylidene-acetophenone, 2·03 (hence *trans*); $CHPh{:}CBr{\cdot}CO_2Et$ (from acid, m.p. 131°), 2·25 (from acid, m.p. 126°), 2·80; Et-, 1·75, Et *p*-nitro-, 4·58, Me *p*-bromo-β-phenylpropionate, 2·39; $NO_2{\cdot}C_6H_4{\cdot}C{:}C{\cdot}CO_2Et$, 3·54 (hence straight structure); ω-nitro-, 4·48, ω-chloro-, 1·40, ω-bromo-, 1·51, ω-ethoxy-styrene, 1·68.

F. R. G.

**Use of paramagnetism as a test for free radicals.** F. L. Allen and S. Sugden (J.C.S., 1936, 440—441).—Solid $NPh_2{\cdot}N{\cdot}C_6H_2(NO_2)_3$, $(p\text{-}NO_2{\cdot}C_6H_4)_3C$, and $CPh_2{\cdot}OK$ are strongly paramagnetic and hence consist largely of free radicals. Solid 10 : 10′-bis-5 : 10-dihydrophenarsazine and $CSPh_2$ are diamagnetic, hence the former probably contains no free radical and the latter may be a free diradical.

F. R. G.

**Autoxidation of substituted difluoryls and dixanthyls.** H. W. Scherp (J. Amer. Chem. Soc., 1936, 58, 576—580).—Autoxidation of 9 : 9′-diphenyl- (I), 9 : 9′-*di*-p-*tolyl*- (II), m.p. 216° (from 9-chloro-9-*p*-tolylfluorene, m.p. 96·5°, and Cu-bronze in $N_2$), 9 : 9′-didiphenylyl- (III), and 9 : 9′-dianisyl- (IV) -9 : 9′-difluoryls in *s*-$C_2H_2Cl_4$ (usually 0·01*M* solution) at 0° and 25° occurs principally by oxidation of the undissociated mol. and to a small extent by oxidation of the free radical. The rate for (I) is not affected by quinol (0·1 or 1%) or change in concn. With one exception, the ratio $k_{O_2}/k_{\mathrm{air}}$ is lower at 0° than at 25°. There is no parallelism between the rate of autoxidation [viz., (III) < (IV) < (II) < (I)] and degree of dissociation into free radicals [viz., (II) < (I) < (III) < (IV); determined in EtOBz and $N_2$ at 70°]. Autoxidation of dimethyl-, di*iso*amyl-, and dibenzyl-dixanthyls at —11·2° to 50° is dependent (in the early stages of the reaction) on slow dissociation into free radicals and subsequent rapid oxidation (cf. Conant and Evans, A., 1929, 934).

H. B.

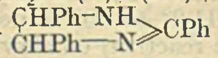
**Rubenes. Isomerisation of diphenylbis-*p*-bromophenylrubene into the corresponding pseudo-derivatives.** L. Enderlin (Compt. rend., 1936, 202, 495—497; cf. A., 1929, 549; this vol.,

462).—Diphenylbis-*p*-bromophenylrubene when treated in $C_6H_6$ with $H_2SO_4$ yields irreversibly two *isomerides*, m.p. 340° and m.p. 240—245° and m.p. 295° after resolidification, separable by means of $CS_2$.
H. G. M.

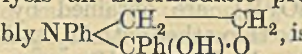
**Reversible oxidisability of organic compounds: dihydroxide of diphenylbis-(*p*-bromophenyl)-rubene.** L. Enderlin (Compt. rend., 1936, **202**, 1188—1190; cf. this vol., 600).—Prolonged oxidation of diphenylbis-*p*-bromophenylrubene in $C_6H_6$ with 0·1% $KMnO_4$ at room temp. affords *dihydroxydihydrodiphenylbis-*(p-*bromophenyl*)*rubene*, $C_{42}H_{26}Br_2(OH)_2$, decomp. at 230° (block), which is reduced (Fe–AcOH) quantitatively to the rubene, and at 220° loses $1H_2O$ to give a *monoxide*, $C_{42}H_{26}Br_2O$. Boiling AcOH or cold $H_2SO_4$ removes $2H_2O$ to give $C_{42}H_{24}Br_2$, which exhibits a violet fluorescence. J. L. D.

**Mechanism of isomerisation of cyclic amines. Action of potassium hydroxide on nitroso*cyclo*propylcarbamide.** V. P. Golmov (J. Gen. Chem. Russ., 1935, **5**, 1562—1565).—*cyclo*Propylamine and KCNO are dissolved in $H_2O$, the solution is evaporated to dryness at 100°, and the residue is extracted with EtOH, when cyclo*propylcarbamide* (I), m.p. 123—124°, is obtained. (I) in aq. $H_2SO_4$ and $NaNO_2$ at 0° afford *nitroso*cyclo*propylcarbamide*, m.p. 86° (decomp.), which is converted, probably by way of diazo*cyclo*propane, into $CH_2{:}CH{\cdot}CH_2{\cdot}OH$ by aq. KOH at 0°. R. T.

**Transposition of *N*-arylformimino-ethers, OEt·CH:NR.** M. Grunfeld (Bull. Soc. chim., 1936, [v], **3**, 668—674).—When passed over infusorial earth at 200°/17 mm., NPh:CH·OEt is largely unchanged; at 300°/15 mm., it gives EtOH, PhNC, and PhCN, whereas at 400°/65 mm. EtOH and PhCN are formed exclusively. $o$-$C_6H_4Me{\cdot}N{:}CH{\cdot}OEt$ is unchanged at 180°/13 mm., gives EtOH, $o$-$C_6H_4Me{\cdot}NC$, and $o$-$C_6H_4Me{\cdot}CN$ at 300°/16 mm., and EtOH and $o$-$C_6H_4Me{\cdot}CN$ at 400°/40—50 mm. $p$-$C_6H_4Me{\cdot}N{:}CH{\cdot}OEt$ at 300°/18—25 mm. affords unchanged material, EtOH, $p$-$C_6H_4Me{\cdot}NC$, and $p$-$C_6H_4Me{\cdot}CN$. Contrary to Wislicenus, diphenylformamidine is not produced when NPh:CH·OMe or NPh:CH·OEt is heated in a sealed tube at 230—240°. *Ethoxymethylene-*m*-toluidine*, from $m$-$C_6H_4Me{\cdot}NH_2$ and $CH(OEt)_3$ at 125° and subsequently at 190—210°, has b.p. 84°/2 mm. H. W.

**Mechanism of amination by means of sodamide. I. Preparation of substituted amidines.** A. V. Kirsanov and J. N. Ivaschtschenko (J. Gen. Chem. Russ., 1935, **5**, 1494—1505).—NPh:CHPh (I) in PhMe and $NaNH_2$ (II) at 120° react as follows: (I)+(II) → $NH_2{\cdot}CHPh{\cdot}NPhNa$ → $NH_2{\cdot}CPh{:}NPh$ (III)+NaH → NHNa·CPh:NPh (IV)+2H; (I)+2H → $NHPh{\cdot}CH_2Ph$ (V); (III)+(II) → (IV)+$NH_3$; 3(I)+$2NH_3$ →  $\begin{array}{l}\text{CHPh–NH}\\ \text{CHPh—N}\end{array}\!\!\geqslant\text{CPh}$ (VI)+$3NH_2Ph$; (VI) undergoes further conversion into lophine (VII). The yields of final products isolated were $NH_2Ph$ 12·0, (III) 19·6, (V) 14·9, and (VIII) 12·8%; the corresponding products and yields obtained when benzylidine-*p*-toluidine is substituted for (I) are *p*-toluidine 22·6, *p*-tolylbenzamidine 22·6, benzyl-*p*-toluidine 20·6, and (VII) 12·3%, whilst piperonylideneaniline yields the N-*phenylamidine* of piperonylic acid, m.p. 138—139°, and piperonylaniline. It is considered that the above mechanism also applies to the reaction of amination of $C_5H_5N$ by (II). R. T.

**Regulated hydrolysis of acetyl derivatives of reducing sugars.** M. Frèrejacque (Compt. rend., 1936, **202**, 1190—1192).—Glucose β-penta-acetate (I) in 95% EtOH containing some AcOH with $p$-$C_6H_4Me{\cdot}NH_2$ at room temp. affords β-tetra-acetylglucosidyl-*p*-toluidide (cf. A., 1928, 870). With $NH_2Ph$, (I) similarly affords a mixture of the anilides of the α- and β-tetra-acetates. The following are prepared: *α-tetra-acetylglucosidylanilide*, m.p. 143°; β-*tetra-acetylglucosidylacetyl-anilide*, m.p. 100°, -p-*toluidide*, m.p. 142°, -p-*bromoanilide*, m.p. 134°; α-, m.p. 197°, and β-*hepta-acetyl-lactosidyl-anilide* (I), m.p. 152°, and -p-*toluidide*, m.p. 202°; β-*hepta-acetylmaltosidyl-anilide* (II), m.p. 205°, and -p-*toluidide*, m.p. 182°; β-*hepta-acetylcellobiosidyl-anilide* (III), m.p. 218°, and -p-*toluidide*, m.p. 215°. (I), (II), and (III) show mutarotation and are easily hydrolysed, but after acetylation, they neither mutarotate nor are they easily hydrolysed. J. L. D.

**Attempted cyclisation of *N*-β-hydroxyethylaniline, and its benzoyl derivatives.** P. P. Schorigin and V. N. Belov (J. Gen. Chem. Russ., 1935, **5**, 1707—1717).—Attempts to obtain dihydroindole by the dehydration of $NHPh{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ (I) (*picrate*, m.p. 124—125°), under different conditions (passing the vapour in a stream of $CO_2$ over kaolin at 450—520°, heating with $H_2C_2O_4$, $AlCl_3$, or Na), were unsuccessful. A small amount of N-*vinylaniline*, m.p. 66—67·5° (*Bz* derivative, m.p. 191—192°), was obtained by heating with Na for 2 hr. at 260—280°. The $Bz_2$ derivative of (I) yields the *O*-monobenzoate (II) [*picrate*, m.p. 150°; N-*Me* derivative, m.p. 46—48° (*picrate*, m.p. 163—164°)] of (I) when hydrolysed with EtOH–KOH; under very mild conditions of hydrolysis an intermediate product, m.p. 74—75°, probably  $\text{NPh}\!<\!\begin{array}{l}\text{CH}_2\text{——CH}_2\\ \text{CPh(OH)·O}\end{array}$, is obtained. The *N*-Bz derivative of (I) readily undergoes conversion into (II).
R. T.

**Rhodanisation of organic compounds.** S. A. Zaboev (J. Gen. Chem. Russ., 1935, **5**, 1607—1610).—$p$-$SCN{\cdot}C_6H_4{\cdot}NMe_2$ (I) is obtained in good yield from $NPhMe_2$ (II), $NH_4CNS$, and $CaOCl_2$ in aq. AcOH, at room temp., or by passing $Cl_2$ at −10° into an aq. AcOH solution of (II) and KCNS. (I) is converted into $(NMe_2{\cdot}C_6H_4{\cdot}S{\cdot})_2$ by boiling with aq. KOH. 5 : 1 : 2-$CNS{\cdot}C_6H_3Me{\cdot}NH_2$ and $p$-$CNS{\cdot}C_6H_4{\cdot}OH$ have been prepared similarly from *o*-toluidine and PhOH, respectively. R. T.

**Rearrangement of carbamyl-sulphones and -sulphides.** W. J. Evans and S. Smiles (J.C.S., 1936, 329—331).—2-*Nitrophenyl-thioacetanilide*, m.p. 159—160°, is oxidised to -*sulphonylacetanilide*, m.p. 151—152°, which undergoes rearrangement (NaOH) to 2-nitro-*N*-acetyldiphenylamine. Similarly, 2-*nitrophenyl-sulphonylaceto-*, m.p. 207°, obtained from -*thioaceto-*m*-nitroanilide*, m.p. 216—217°, is rearranged to 2 : 3′-dinitrodiphenylamine. 2-*Nitrophenylsulphonyl-*, m.p. 155—156°, obtained from -*thio-acetamide*, m.p. 178—179°, does not undergo rearrangement.

β-2-*Nitrophenyl-thiopropionanilide*, m.p. 166°, obtained from the corresponding *acid*, m.p. 147°, is oxidised to the -*sulphonyl* compound, m.p. 186—187°, neither sulphide nor sulphone undergoing rearrangement, possibly owing to the steric relationships. 2-o-*Nitrophenylthiobenz-amide*, m.p. 164°, and -*anilide*, m.p. 127—128°, obtained from the acid chloride, are oxidised, respectively, to 2-o-*nitrobenzenesulphonylbenz-amide*, m.p. 193—194°, and -*anilide*, m.p. 184°. Rearrangement, followed by methylation, of these compounds gives, respectively, 2-*methylthiolbenzo*-o-*nitroanilide*, m.p. 111°, and -2′-*nitrodiphenylamide*, m.p. 146—147°, and 2-*methylsulphonylbenzo*-o-*nitroanilide*, m.p. 221°, and -2′-*nitrodiphenylamide*, m.p. 206°. F. R. S.

**3-Nitro-4-aminodiphenylmethane and its derivatives.** W. A. Waters (J.C.S., 1935, 1875).—4-Acetamidodiphenylmethane when treated at 25° during 1 hr. with $Cu(NO_3)_2,3H_2O$ in $Ac_2O$ (Menke's method) affords 3-*nitro*-4-*acetamidodiphenylmethane* (I), m.p. 99°, also obtained when a warm solution of 4-aminodiphenylmethane in $Ac_2O$ is similarly treated with $Cu(NO_3)_2,3H_2O$–$Ac_2O$, and hydrolysed by $H_2SO_4$–EtOH to 3-*nitro*-4-*aminodiphenylmethane*, m.p. 78° (5-*Br*-derivative, m.p. 71°). (I) with $H_2SO_4$–AcOH–$HNO_3$ yields 3 : 4′-dinitroacetamidodiphenylmethane (A., 1933, 1044), also obtained together with some 3 : 5-*dinitro*-4-*acetamidodiphenylmethane*, m.p. 81—82°, when (I) is treated by Menke's method. H. G. M.

**Optical activity in relation to tautomeric change. V. Kinetic status of ionic intermediates in prototropy.** S. K. Hsü, C. K. Ingold, and C. L. Wilson (J.C.S., 1935, 1778—1785).—The velocity coeffs. and equilibrium consts. of isomerisation of *dl*-benzhydrylidene-α-phenylethylamine (I) and of *dl*-benzylidene-*p*-phenylbenzhydrylamine (II) have been determined and compared, respectively, with the rate of racemisation of optically active (I) and the rate of mutarotation of the system optically active (II)+its isomeride. The results accord with the view that loss of optical activity does not occur in any reversibly formed intermediate state in the isomerisation process (cf. A., 1934, 260), and that the ionisation products of these systems do not become kinetically free during isomerisation. Prototropy in the methyleneazomethine system therefore occurs by a termol. mechanism of the type proposed by Lowry (A., 1927, 1150), the bimol. mechanism (cf. A., 1926, 939) being restricted to more acid systems such as carboxyl ([H]·O·C:O) and acetone ([H]·O·C:C). p-*Phenylbenzophenone*-2 : 4-*dinitrophenylhydrazone* has m.p. 217—217·5°. H. G. M.

**Preparation of Freund's acid from α-naphthylamine-3 : 6 : 8-trisulphonic acid.** G. I. Ostroshinskaja (Anilinokras. Prom., 1935, 5, 138—143).—1 : 3 : 6-$NH_2·C_{10}H_5(SO_3H)_2$ (I) is obtained in 93% yield by boiling a mixture of 1 : 3 : 6 : 8-$NH_2·C_{10}H_4(SO_3H)_3$, aq. NaOH, and Zn dust for 7 hr. The dichloride of (I) has m.p. 149° (lit. 157°). R. T.

**Determination and purification of β-naphthylamine in the presence of α-naphthylamine, and properties of some sulphonyl derivatives.** H. H. Hodgson and E. W. Smith (J.C.S., 1935, 1854—1856).—The solubilities of *p*-toluenesulphon-α- (I) and -β-naphthalide (II) in 20% aq. NaOH at 16° are 125 g. and 3 g. per litre, but in 2% aq. KOH are 85 g. and 66 g. per litre, respectively. (II) is completely pptd. by ≮ 10% aq. NaOH from a solution of (I) and (II) in 2% NaOH, provided [(I)] is ≯ 20%, thus permitting the determination of β-$C_{10}H_7·NH_2$ (III) in presence of α-$C_{10}H_7·NH_2$ (IV). (III) may be purified from (IV) by pptn. from $C_6H_6$ by HCl, or by neutralising an acid solution of the mixture, the hydrochloride of (III) or (III) itself being pptd. first, respectively. $Na^{\cdot}$ can easily be detected when $[Na^{\cdot}]$ is $> 2\%$ by addition of (II)–KOH–$H_2O$. 2 : 4 : 1-$(NO_2)_2C_{10}H_5·NH_2$ (improved prep.) has m.p. 242° (lit. 239°). The following are described: *Na* salt, m.p. 370°, of (II); *Na*, m.p. 256°, *Na* (+$H_2O$), *Na* (+4$H_2O$), m.p. 85°, *K*, m.p. 232°, and *K* (+2$H_2O$) salts of *m*-nitrobenzenesulphon-α-naphthalide; *m-nitrobenzenesulphon*-β-*naphthalide*, m.p. 166·5° [*Na*, m.p. 290°, *Na* (+$H_2O$), and *Na* (+4$H_2O$), m.p. about 77°; *K*, m.p. 240°, *K* (+$H_2O$), *K* (+3$H_2O$), m.p. about 70°; *Ba*, m.p. about 280° (with charring), and *Ba* (+2$H_2O$) salts]. H. G. M.

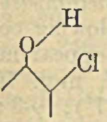
**Preparation and properties of some 1 : 2-diamino*cyclo*hexanes.** F. M. Jaeger and J. A. van Dijk (Proc. K. Akad. Wetensch. Amsterdam, 1936, 39, 384—393).—2-Methyl*cyclo*hexanone with $Et_2C_2O_4$ and NaOEt–EtOH at −15° affords its 6-*glyoxylic acid* and the corresponding *Et* ester, converted by heating at 210—220° into *Et* 2-*methyl*cyclo*hexanone*-6-*carboxylate*, b.p. 115—116·5°/12—13 mm., converted by 6% aq. KOH–$NaNO_2$ and 30% $H_2SO_4$ at room temp. into 6-*oximino*-2-*methyl*cyclo*hexanone* (I), m.p. 167° (decomp.), a (?) stereoisomeric *oxime* (II), m.p. 65°, and an oily mixture of oximes. (I) with $NH_2OH$,HCl–NaOMe–MeOH affords 2 : 3-*dioximino*-1-*methyl*cyclo*hexane* (III), m.p. 167° [differs in its reactions from that obtained by Wallach *et al.* (A., 1924, i, 862), which was probably a mixture of (III) and (IV)]; (II) similarly gives a *dioxime* (IV), m.p. 140°. Reduction of (III) with Na–boiling EtOH affords 2 : 3-*diamino*-1-*methyl*cyclo*hexane*, b.p. 84°/12 mm. (isolated as its *hydrochloride* +2$H_2O$), also obtained, together with 3-*amino*-1-*methyl*cyclo*hexane*, b.p. 41°/12 mm. (*Bz* derivative, m.p. 106°), by similar reduction of the dioxime obtained from the oily mixed oximes. By similar series of reactions are obtained 2-*oximino*cyclo*hexanone* (from Et *cyclo*hexanone-2-carboxylate), the *dioxime*, m.p. 187—189°, and trans-1 : 2-*diamino*cyclo*hexane*, b.p. 79—81°/15 mm. (resolvable); *Et* 3-*methyl*cyclo*hexanone*-6-*carboxylate*, b.p. 118—120°/13 mm., 6-*oximino*-3-*methyl*-cyclo*hexanone*, m.p. 159°, the *dioxime*, m.p. 180—181° (also obtained from *Et* 4-*methyl*cyclo*hexanone*-6-*carboxylate*, b.p. 113—115°/13 mm.), and 3 : 4-*diamino*-1-*methyl*cyclo*hexane*, b.p. 81·5°/13 mm. 3 : 4-Diamino-1-methyl-4-*iso*propyl*cyclo*hexane (diaminomenthane), b.p. 110—113°/12 mm., is obtained by a modification of the method of Konovalov *et al.* (A., 1898, i, 530). Crystallographic data and reactions with metallic salts are given for many of the above compounds. J. W. B.

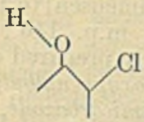
**Derivatives of 4 : 4′-diaminodiphenylmethane.** G. D. Parkes and R. H. H. Morley (J.C.S., 1936, 315—317).—Bromination of 4 : 4′-diacetamidodiphenylmethane gives the 3 : 3′-*$Br_2$*-derivative, m.p. 198°, hydrolysed to 3 : 3′-*dibromo*-4 : 4′-*diaminodiphenylmethane dihydrochloride*, m.p. 285° (decomp.), from which is prepared through the tetrazo-compound the corresponding -4 : 4′-*dihydrazinodiphenylmethane dihydrochloride*, m.p. 279° (decomp.). 3 : 3′-*Dibromo*-4 : 4′-*dibenzamidodiphenylmethane* has m.p. 217°. The following have been prepared from the appropriate dihydrazine and the carbonyl compound: 4 : 4′-*bis*-o-, m.p. 189°, m-, m.p. 192°, and -p-*nitrobenzylidenehydrazino*-, m.p. 218°; 4 : 4′-*bis-salicylidenehydrazino*-, m.p. 252°, -β-*phenylethylidenehydrazino*-, m.p. 174°, and -γ-*phenyl-α-methylallylidenehydrazino*-, m.p. 222°; 3 : 3′-*dibromo*-4 : 4′-*bis-benzylidenehydrazino*-, m.p. 165°, -o-*nitrobenzylidenehydrazino*-, m.p. 234°, m-, m.p. 278°, and p-, m.p. 255° (decomp.), -*salicylidenehydrazino*- m.p. 236° (decomp.), and -p-*hydroxybenzylidenehydrazino-diphenylmethane*, m.p. 238° (decomp.). F. R. S.

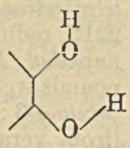
**Salt formation of homonuclear naphthalene derivatives.** H. H. Hodgson and R. L. Elliott (J.C.S., 1935, 1850—1854).—2-Nitroaceto-1-naphthalide (I) when treated with AcOH–$Cl_2$ at 100° (30 min.) yields its 4-*Cl*-derivative (II), m.p. 219°, hydrolysed to 4-*chloro-2-nitro-α-naphthylamine* (III), m.p. 202°. This when treated with $H_2SO_4$–$NaNO_2$ below 20° and then heated with EtOH (water-bath, 90 min.) affords 1-*chloro-3-nitronaphthalene*, m.p. 127°, which when heated with $SnCl_2$–HCl–EtOH gives 4-*chloro*-β-*naphthylamine stannichloride*, which with 2% aq. NaOH gives 4-*chloro*-β-*naphthylamine*, m.p. 68°. The corresponding 4-Br-derivative (*stannichloride*; *Ac* derivative, m.p. 186·5°) was similarly prepared. 2 : 1-$NO_2\cdot C_{10}H_6\cdot NH_2$ and $Hg(OAc)_2$–boiling AcOH yield 2-*nitro-α-naphthylamine* 4-*mercuriacetate*, m.p. 242° [the corresponding *mercurichloride*, m.p. 289°, *mercuribromide*, m.p. 248°, *mercuri-iodide*, m.p. 237°, and *mercurihydroxide*, m.p. above 360° (decomp.)], which with $Cl_2$ or Br in AcOH gave the corresponding 4-Cl- or 4-Br-derivative, respectively, and when boiled with KI–I–$H_2O$ yields the 4-I-derivative, m.p. 195·5° (lit. 192—193°). This when deaminated and subsequently reduced ($SnCl_2$–EtOH) affords 4-*iodo-2-naphthylamine*, m.p. 76° (*Ac*, m.p. 201°, and *Bz* derivative, m.p. 145°), as the *stannichloride*. 4 : 2 : 1-$NO_2\cdot C_{10}H_5Cl\cdot NH_2$ when boiled with hydrated $SnCl_2$, EtOH, and HCl gives 2-*chloro*-1 : 4-*naphthylenediamine monohydrochloride* (IV), diazotisation of which proceeded normally at first but subsequently the diazo-solution deposited a deep purple powder, m.p. above 360° (decomp.). The *diamine*, m.p. 114° (NN′-*$Ac_2$*, m.p. 314°, and NN′-*$Bz_2$* derivative, m.p. 255°), obtained from (IV), is readily oxidised by 2% alkaline $KMnO_4$ to 2-chloro-1 : 4-naphthaquinone. Similarly 2-chloro-4-nitroaceto-1-naphthalide when reduced (hydrated $SnCl_2$–HCl–EtOH) affords 2-*chloro*-1-N-*acetyl*-1 : 4-*naphthylenediamine*, m.p. 215°, as the *stannichloride*, from which the base was obtained with NaOH. The following were prepared by similar methods: 2-*bromo*-1 : 4-*naphthylenediamine*, m.p. 110° (*stannichloride*; *monohydrochloride*; *$Ac_2$*, m.p. 318°, and *$Bz_2$* derivative, m.p. 259°), oxidised to 2-bromo-1 : 4-naphthaquinone; 2-*bromo-4-nitroaceto*-1-*naphthalide*, m.p. 239° (obtained from the amine), with boiling 20% aq. NaOH affords 2-*bromo-4-nitro-α-naphthol*, m.p. 236°, and is reduced to 2-*bromo*-1-N-*acetyl*-1 : 4-*naphthylenediamine*, m.p. 217° (*stannichloride*); 2-*iodo*-1 : 4-*naphthylenediamine*, m.p. 119° (*monohydrochloride*; NN′-*$Ac_2$*, m.p. 322°, and NN′-*$Bz_2$* derivative, m.p. 262°), oxidised by alkaline 2% $KMnO_4$ to 2-*iodo*-1 : 4-*naphthaquinone*, m.p. 120°; 2-*iodo*-4-*nitroaceto*-1-*naphthalide*, m.p. 222° (prepared by heating 4-nitro-α-naphthylamine 2-mercuriacetate with $Ac_2O$ and boiling the resulting 4-*nitroaceto*-1-*naphthalide* 2-*mercuriacetate*, m.p. 270°, with aq. KI–I), with boiling 20% aq. NaOH affords 2-*iodo*-4-*nitro-α-naphthol*, m.p. 229°, and is reduced to 2-*iodo*-1-N-*acetyl*-1 : 4-*naphthylenediamine*, m.p. 235° (*stannichloride*); 4-*chloro*-1 : 2-*naphthylenediamine* (V), m.p. 95° (*monohydrochloride*; with $Ac_2O$ at 35—40° gives the 2-N-*Ac* derivative (VI), m.p. 235°), obtained from (III); 4-*chloro*-1-N-*acetyl*-1 : 2-*naphthylenediamine* (VII), m.p. 243° (*stannichloride*), obtained from (II), yields (with $Ac_2O$) the *$Ac_2$* derivative, m.p. 174°, of (V), not obtained from (VI) and boiling $Ac_2O$; 4-*chloro*-1 : 2-*naphthaquinone*, m.p. 188° [readily obtained by air-oxidation of (VII)]; 4-*bromo*-1 : 2-*naphthylenediamine* (VIII), m.p. 97° (*monohydrochloride*; 2-N-*Ac* derivative, m.p. 225°, obtained from the base and boiling $Ac_2O$). (I) with Br–AcOH above 45° yields 4-*bromo-2-nitroaceto*-1-*naphthalide*, m.p. 239°, reduced to 4-*bromo*-1-N-*acetyl*-1 : 2-*naphthylenediamine*, m.p. 248° (*stannichloride*), converted by boiling $Ac_2O$ into the NN′-*$Ac_2$* derivative, m.p. 225°, of (VIII), not obtained from the 2-*N*-Ac isomeride and $Ac_2O$. The following were similarly prepared: 4-*iodo*-1 : 2-*naphthylenediamine*, m.p. 98° [*monohydrochloride*; 2-N-*Ac*, m.p. 238°, and NN′-*$Ac_2$* derivative, m.p. 167°; 1-N-*Ac* derivative, m.p. 271° (*stannichloride*)]. The stability of the salts of the foregoing bases is discussed. H. G. M.

**Decomposition of azo-compounds by mineral acids.**—See B., 1936, 311.

**Interpretation of infra-red absorption of organic compounds containing hydroxyl and imino-groups.** L. Pauling (J. Amer. Chem. Soc., 1936, 58, 94—98).—The single sharp absorption peak (in the region 6200—7200 cm.$^{-1}$) exhibited by 21 of the 32 substances investigated by Wulf and Liddel (A., 1933, 1102; 1935, 1189) indicates that the OH or NH groups in the dissolved mols. have nearly the same characteristic frequencies; in the mols. containing 2 or more OH or NH, there is little interaction between such groups. The C·O in phenols has some C:O character (resulting from resonance with a structure such as $\cdot\overset{-}{C}_2\cdot C_1{:}\overset{+}{O}-H$), thus tending to cause the H atom to lie in the plane of the rest of the mol. PhOH and *s*-$C_6H_2Cl_3\cdot OH$ can thus assume either of two equiv. configurations (cf. below); the OH frequency for *s*-$C_6H_2Cl_3\cdot OH$ (6890 cm.$^{-1}$) will, however, owing to the attraction of the (+)-H by the (−)-Cl, be < that for PhOH (7050 cm.$^{-1}$) (cf. Badger, A., 1934, 477). *o*-$C_6H_4Cl\cdot OH$ can exist in *cis*- (*A*) and *trans*- (*B*) forms; owing to the stabilising effect of the tendency for interaction of H and Cl, the former should be the more stable and predominate. The


(*A.*)


(*B.*)


(*C.*)

curve for *o*-$C_6H_4Cl{\cdot}OH$ contains two peaks (large at 6910, small at 7050 cm.$^{-1}$) and indicates the presence of about 91% of (*A*) and 9% of (*B*). The free energy difference of (*A*) and (*B*) is about 1400 g.-cal. per mol. *o*-$C_6H_4(OH)_2$ has structure (*C*); the two (equal) peaks at 6970 and 7060 cm.$^{-1}$ represent *cis*- and *trans*-OH, respectively. Weak chelation is considered to occur in Et lactate and tartrate and benzoin, but not in *o*-$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$ and $OH{\cdot}CH_2{\cdot}CH_2{\cdot}OAc$. The splitting of the :NH-absorption for pyrrole (and NHAcPh) is probably due to the existence (in solution) of mols. of (mainly) coplanar (H of NH in plane of ring) and non-coplanar forms. Carbazole and tetraphenylpyrrole have coplanar configurations. The tendency for $\cdot CO \leftarrow HN\cdot$ chelation (as in phenanthraquinoneimine) is much $< \cdot CO \leftarrow HO$. H. B.

**Chloro-alkylation of anisole; synthesis of vinylanisole.** R. Quelet (Compt. rend., 1936, **202**, 956—958).—Chloro-ethylation is effected by saturating at 0° with HCl a mixture of 1 mol. of anisole, 1 mol. of paraldehyde, and 100 g. of conc. HCl. The product is washed with $H_2O$ and extracted with light petroleum. Warming with $C_5H_5N$ gives a mixture of *o*- and *p*-vinylanisole, b.p. 91—94° 16 mm., in 40% yield. αα-Di-*p*-anisylethane is also formed. α-Chloropropylanisole is similarly obtained in 20% yield with $H_3PO_4$ as catalyst, and α-chlorobutylanisole in 50% yield with HCl as catalyst; these yield respectively a mixture of anethole and *o*-methoxy-$\Delta^{\alpha}$-propenylbenzene, and of *o*- and *p*-methoxy-$\Delta^{\alpha}$-butenylbenzene. P. G. M.

**Halogenation of phenolic ethers and anilides. V. Alkyl and ω-substituted-alkyl ethers. VI. Benzyl and substituted-benzyl ethers.** B. Jones (J.C.S., 1935, 1831—1835, 1835—1840).—V. The velocity coeffs. of chlorination at 20° of a no. of ethers of the type $C_6H_4X{\cdot}OR$ (X=*o*- and *p*-$CO_2H$, hal.; R=alk., $\cdot[CH_2]_n{\cdot}Br$, $\cdot[CH_2]_n{\cdot}Ph$) in AcOH containing 1% $H_2O$ have been determined. The reactivity of *n*-alkyl ethers is const. from R=Pr to R=heptyl, but is slightly lower when R=octyl and cetyl. ω-Br- and ω-Ph substituents depress the reactivity, the effect decreasing with increasing chain-length. The following *ethers* have been prepared: p-*chlorophenyl* n-*amyl*, b.p. 132—133°/12 mm., n-*hexyl*, b.p. 172°/34 mm., n-*heptyl*, b.p. 162°/14 mm., and *cetyl*, m.p. 48°; p-*bromophenyl cetyl*, m.p. 49°; o-*chlorophenyl* $Pr^{\alpha}$, b.p. 119°/26 mm., $Pr^{\beta}$ (I), b.p. 93°/12 mm., $Bu^{\alpha}$, b.p. 117°/13 mm., n-*amyl*, b.p. 117°/13 mm.; p-*bromophenyl γ-bromopropyl*, m.p. 49·5°, b.p. 169°/12 mm. (by-product *trimethylene glycol bis*-p-*bromophenyl ether*, m.p. 143°). *p*-β-*Phenylethoxybenzoic acid* has m.p. 160°, and p-γ-*phenylpropoxybenzoic acid* has m.p. 166°.

VI. The velocity coeffs. of chlorination at 20° of a no. of ethers of the type $C_6H_4X{\cdot}OR$ (X=*o*- and *p*-$CO_2H$, Cl, Br; R=$\cdot CH_2Ph$, $\cdot CH_2{\cdot}C_6H_4Y$ where Y=*o*-, *m*-, and *p*-Me, -F, -Cl, -$NO_2$, and *m*- and *p*-Br) in AcOH containing 1% $H_2O$ have been determined (cf. A., 1932, 26). The majority (including those of the preceding paper) accord with the view that each of the groups X and R contributes a characteristic additive quota to the activation energy of chlorination. (I) and ethers of salicylic acid give anomalous results. The order of reactivity for *p*-substituents in the $\cdot CH_2Ph$ radical is Me > H > F > Cl > Br > $NO_2$; in the *m*-position the halogens show almost identical effects. The reactivity of the *o*- and *m*-halogenobenzyl ethers is < that of the *p*-compounds. The results indicate a mesomeric effect in the order F > Cl > Br. The following have been prepared:—p-*chlorophenyl ethers*: m-, b.p. 223—225°/12 mm., and p-, m.p. 60°, -*fluoro-*; o-, b.p. 191°/12 mm., m-, b.p. 222—224°/12 mm., and p-, m.p. 60°, -*chloro-*; m-, m.p. 43°, and p-, m.p. 93°, -*bromo-*; p-*methyl-*, m.p. 97°, and o-*nitro-benzyl*, m.p. 73°; o-*chlorophenyl ethers*: p-*fluoro-*, m.p. 35°, b.p. 170°/12 mm., p-*chloro-*, m.p. 69°, p-*methyl-*, m.p. 76°, and o-*nitro-benzyl*, m.p. 84·5°; p-*bromophenyl ethers*: p-*chloro-*, m.p. 98°, and p-*methyl-benzyl*, m.p. 105°; o-*bromophenyl ethers*: p-*chloro-*, m.p. 69°, and o-, m.p. 107°, and m-, m.p. 100°, -*nitro-benzyl*. p-(p′-*Fluorobenzyloxy*)*benzoic acid* has m.p. 213°, the corresponding p′-*chloro-acid*, m.p. 218°, and p′-*bromo-acid*, m.p. 231°. p-(p′-*Methylbenzyloxy*)*benzoic acid* has m.p. 212°, and the corresponding m′-*methyl-acid*, m.p. 157°. p-(m′-*Fluorobenzyloxy*)*benzoic acid* has m.p. 194°, the corresponding m′-*chloro-acid*, m.p. 194°, and m′-*bromo-acid*, m.p. 202°. p-(o′-*Fluorobenzyloxy*)*benzoic acid* has m.p. 181°, the corresponding o′-*chloro-acid*, m.p. 189°, and the o′-*methyl-acid*, m.p. 169°. o-*Benzyloxybenzoic acid* has m.p. 77° and o-(p′-*fluorobenzyloxy*)-*benzoic acid*, m.p. 87°, the corresponding p′-*chloro-acid*, m.p. 115°, and the p′-*methyl-acid*, m.p. 111°.
H. G. M.

***o*-Nitrophenylsulphenates of phenols.** E. K. Learmonth and S. Smiles (J.C.S., 1936, 327—328).—The 2-nitrophenylsulphenates of the phenols are obtained from 2 : 1-$NO_2{\cdot}C_6H_4{\cdot}SCl$ and the Na phenoxide and converted into the OH-sulphides with HCl. 2-*Nitrophenylsulphenates* of *m*-4- (I), m.p. 85°, and *m*-5-xylenol (II), m.p. 74°, 2-chloro-, m.p. 118—120°, and 2 : 6-dichloro-*m*-5-xylenol, m.p. 125—127°, 5-chloro-*p*-2-xylenol, m.p. 120° and ψ-cumenol, m.p. 103°, have been prepared. (I) gives 2-nitro-2′-hydroxy-3 : 5′-dimethyldiphenyl sulphide (*Me ether*, m.p. 79°). 2-*Nitro-4′-hydroxy-2′* : 6′-*dimethyldiphenyl sulphide*, m.p. 154° [from (II)] (*Ac* derivative, m.p. 121°; *Me ether*, m.p. 130°), is oxidised to the *sulphone*, m.p. 218° (decomp.). 3′-Chloro-2-nitro-6′-hydroxy-2′ : 4′-dimethyldiphenyl sulphide forms an *Ac* derivative, m.p. 145°, and a *Me ether*, m.p. 156°, and 2-nitro-2′-hydroxy-3′ : 5′ : 6′-trimethyldiphenyl sulphide gives an *Ac* derivative, m.p. 135°. F. R. S.

**Benzylation of phenol.** L. McMaster and W. M. Bruner (Ind. Eng. Chem., 1936, **28**, 505—506).—$CH_2PhCl$ dropped slowly into PhOH (10 mols.) at 150°, yields *o*- (52·7%) and *p*- (39·9%) -$CH_2Ph{\cdot}C_6H_4{\cdot}OH$

together with 2 : 4- and 2 : 6-$(CH_2Ph)_2C_6H_3$·OH which are separated in a 40-in. Vigreux column. The effect of varying the temp. and mol. ratio is recorded.

F. R. G.

**Hydrolysis and thermal decomposition of mixed diacyl derivatives of 4-chloro-2-aminothiophenol.** H. P. LANKELMA and E. VOPICKA (J. Amer. Chem. Soc., 1936, **58**, 609—611; cf. A., 1931, 348).—4-*Chloro-2-cinnamamidothiophenyl cinnamate*, m.p. 172—173°, and 4-*chloro-2-phenylacetamidothiophenyl phenylacetate*, m.p. 149°, are hydrolysed (method: *loc. cit.*) to 4-*chloro*-2-*cinnamamidothiophenol*, m.p. 153—155° (*acetate*, m.p. 138°; *benzoate*, m.p. 164—165°), and 4-*chloro-2-phenylacetamidothiophenol* (I), m.p. 126° [*acetate* (II), m.p. 122—123°; *benzoate*, m.p. 161°], respectively. 4-*Chloro-2-acetamidothiophenyl phenylacetate* (III), m.p. 149°, and *cinnamate*, m.p. 142°, and 4-*chloro-2-benzamidothiophenyl phenylacetate*, m.p. 154°, and *cinnamate*, m.p. 122°, are described. Hydrolysis (EtOH–KOH at room temp.) of each pair of isomeric *NS*-diacyl derivatives gives the same *N*-acyl derivative (migration of acyl between S and N thus occurring), which when crystallised from EtOH passes into the corresponding benzthiazole (also formed by thermal decomp. of each pair of isomerides); for the following pairs the first-named group is eliminated on hydrolysis: Ac–$CH_2$Ph·CO·; Ac–cinnamyl; $CH_2$Ph·CO·–Bz; Bz–cinnamyl; Ac–Bz. Thus, (II) and (III) give (I) and then 5-*chloro-2-benzylbenzthiazole*, m.p. 81—82°.

H. B.

**Alkylated phenolic hydroxy-indenes and -indanes. Synthesis involving condensation of diacetone alcohol or pinacol with phenols.** J. B. NIEDERL, V. NIEDERL, and S. REZNEK (J. Amer. Chem. Soc., 1936, **58**, 657—659).—Diacetone alcohol (I) (1 mol.), PhOH (1 mol.), and $ZnCl_2$ (2 mols.) at 180—210° give polymeric 5-*hydroxy*-1 : 1 : 3-*trimethylindene*, b.p. 250—255°/3 mm., m.p. 80—90°, pyrolysis of which affords 10—15% of 5-*hydroxy*-1 : 1 : 3-*trimethylindane* (II), b.p. 263—267°, m.p. 119° [$(NO_2)_2$-, m.p. 112°, and $Br_2$-, m.p. 190°, derivatives; Me ether, an oil (*Br*-derivative, m.p. 69°)], oxidised (conc. $HNO_3$) to 4-hydroxyphthalic acid and anhydride and *m*-OH·$C_6H_4$·COMe. Non-cryst. hydroxytetramethylindanes (not investigated) are similarly formed from the cresols and (I); guaiacol leads to 5-*hydroxy*-(?)-*methoxy*-1 : 1 : 3-*trimethylindane*, b.p. 258—265°. Pinacol and PhOH similarly lead to 5-*hydroxy*-1 : 1 : 2-*trimethylindane*, m.p. 121°. Cryst. products could not be obtained from diacetone glycol (β-methylpentane-βδ-diol). Numerous by-products (*e.g.*, $COMe_2$, mesityl oxide, phenolic and non-phenolic chromans, *p*-$C_6H_4Bu^\gamma$·OH, resins) are also formed in the condensations. (II) appears to possess slight œstrogenic activity.

H. B.

**Condensation of succinic anhydride with phenols and phenolic ethers. Synthesis of derivatives of tetrahydronaphthalene.** P. C. MITTER and S. DE (J. Indian Chem. Soc., 1935, **12**, 747).—PhOMe, succinic anhydride, and $AlCl_3$ in $(·CHCl_2)_2$ give γ-keto-γ-*p*-methoxyphenylbutyric acid [*semicarbazone*, m.p. 185—186° (decomp.)] in good yield (cf. A., 1934, 652). This on Clemmensen reduction gives γ-p-*methoxyphenylbutyric acid*, m.p. 60°, dehydrated by $P_2O_5$ in $C_6H_6$ to 1-*keto*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 61° (*semicarbazone*, m.p. 221°), reduced (Clemmensen) to 1 : 2 : 3 : 4-*tetrahydro*-7-*naphthyl Me ether*, m.p. 146°. The following compounds were similarly prepared and also appear new: γ-*keto*-γ-3 : 4-*dimethoxyphenylbutyric acid*, m.p. 163° (from veratrole) (*semicarbazone*, m.p. 177°); γ-3 : 4-*dimethoxyphenylbutyric acid*, m.p. 61°; 1-*keto*-6 : 7(or 7 : 8)-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 99—100° (*semicarbazone*, m.p. 242—243°); and γ-o-*hydroxyphenylbutyric acid*, m.p. 65—66°.

H. G. M.

**Naphthalene series. IV. Hydrolysis of α-naphthylamine by dilute sulphuric acid.** N. N. VOROSCHCOV and A. V. GUTORKO (J. Gen. Chem. Russ., 1935, **5**, 1581—1585).—Max. yields of α-$C_{10}H_7$·OH are obtained at 200°, taking 1 mol. of $H_2SO_4$ per mol. of α-$C_{10}H_7$·$NH_2$; the concn. of the acid is immaterial.

R. T.

**Diaryls and their derivatives. VIII. Influence of acidity of the medium on interaction of β-naphthol with ferric chloride.** J. S. JOFFE, S. G. KUZNETZOV, and S. LITOVSKI (J. Gen. Chem. Russ., 1935, **5**, 1685—1686).—In the reaction between β-$C_{10}H_7$·OH and aq. $FeCl_3$ the yield of 2 : 2′-dihydroxy-1 : 1′-dinaphthyl falls, and that of 1 : 2-$C_{10}H_6$Cl·OH rises, with increasing [HCl].

R. T.

**Phenanthrene series. I. 2-Methoxy-1-methylphenanthrene.** P. HILL, W. F. SHORT, and (in *part*) (MISS) A. HIGGINBOTTOM. **II. 7-Methoxy-1-methylphenanthrene and a new route to phenanthrene.** W. F. SHORT, H. STROMBERG, and A. E. WILES. **III. 9-Hydroxyphenanthrene.** I. R. SHERWOOD, W. F. SHORT, and J. WOODCOCK (J.C.S., 1936, 317—319, 319—322, 322—324).—I. 1 : 2-$C_{10}H_6$Me·OMe, succinic anhydride, and $AlCl_3$ give β-(2-*methoxy*-1-*methyl*-6-*naphthoyl*)*propionic acid*, m.p. 161—162°, reduced (Hg–Zn) to γ-(2-*methoxy*-1-*methyl*-6-*naphthyl*)*butyric acid*, m.p. 123—123·5°, which with $SnCl_4$–HCl forms 1-*keto*-7-*methoxy*-8-*methyl*-1 : 2 : 3 : 4-*phenanthrene*, m.p. 107° (2 : 4-*dinitrophenylhydrazone*, m.p. 281°). Reduction (Zn–Hg) of the keto-compound affords 7-*methoxy*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 111—112°, dehydrogenated (Se) to 2-*methoxy*-1-*methylphenanthrene*, m.p. 161°, which is demethylated to the 2-*OH*-compound, m.p. 196—197°. 4-Methylphenanthrene (cf. Radcliffe *et al.*, A., 1931, 1282) has m.p. 49—50°.

II. β-$C_{10}H_7$·OMe, succinic anhydride, and $AlCl_3$ in $CS_2$ give β-(2-*methoxy*-1-*naphthoyl*)*propionic acid*, m.p. 136·5—137·5° (*Et* ester, m.p. 41—42°), whilst in $PhNO_2$, a mixture of 1 part of this acid with parts of β-(2-*methoxy*-6-*naphthoyl*)*propionic acid* (I), m.p. 148·5—149° (*Me* ester, m.p. 98°), is formed (cf. Fieser and Peters, A., 1933, 67). The Et ester of (I) and MgMeI, followed by acidification, yield γ-(2-*methoxy*-6-*naphthyl*)-$\Delta^\beta$-*pentenoic acid*, m.p. 171—171·5°, reduced ($PtO_2$–$H_2$) to γ-(2-*methoxy*-6-*naphthyl*)-n-*valeric acid*, m.p. 121·5°, which is dehydrated ($P_2O_5$) to 4-*keto*-7-*methoxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, b.p. 195°/0·8 mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 241° (decomp.)]. Reduction (Zn–Hg) and dehydrogenation (Se) of the cyclic ketone gives 7-*methoxy*-1-*methylphenanthrene*, m.p. 133·5—134·5°, demethylated to the 7-*OH*-compound, m.p. 190—191° [*acetate*, m.p. 135·5—136°, *acetoxyquinone*, m.p. 202—207° (decomp.), and *acetoxyquinoxaline*, m.p. 244·5—246·5°]. Mg *o*-tolyl iodide and 2-methyl*cyclo*hexanone give 1-o-*tolyl*-2-*methyl*cyclo*hexanol*, b.p. 153—154°/14 mm., dehydrogenated (S) to 2 : 2′-dimethyldiphenyl. 2-Methyl*cyclo*hexanone and the Grignard compound of 6-bromo-*m*-tolyl Me ether afford 1-(5′-*methoxy*-o-*tolyl*)-2-*methyl*-$\Delta^1$-cyclo*hexene*, b.p. 154—155°/13 mm., dehydrogenated (HI) to 4-*hydroxy*-2 : 2′-*dimethyldiphenyl*, m.p. 105°.

III. *Et diphenylyl*-2-*acetate*, b.p. 154—155°/4 mm. (from 2-phenyl*cyclo*hexanone, $CH_2Br{\cdot}CO_2Et$, and Zn), with $H_2SO_4$ forms 9-hydroxyphenanthrene. The Grignard compound of 3-bromo-*p*-tolyl Me ether and *cyclo*hexanone afford 1-(4′-methoxy-*m*-tolyl)-$\Delta^1$-*cyclo*hexene, dehydrated ($KHSO_4$) to 1-(4′-*methoxy*-m-*tolyl*)-$\Delta^1$-cyclo*hexene*, b.p. 163°/20 mm., which is oxidised ($BzO_2H$) to the oxide, isomerised to 2-(4′-methoxy-*m*-tolyl)*cyclo*hexanone (*semicarbazone*, m.p. 199—200°). F. R. S.

**Manufacture of pyrene compounds [hydroxypyrenes and their sulphonic acids].**—See B., 1936, 361.

**Preparation of *sec*.-alkyl- and chloro-*sec*.-alkyl-resorcinols.**—See B., 1936, 443.

**Colour reactions of quinol in solid state.** S. J. French and D. J. Saunders (J. Amer. Chem. Soc., 1936, **58**, 689—690).—The colours produced (cf. Maldiney, A., 1914, ii, 681) when solid quinol (I) is mixed with various solid salts depend on the presence of traces of $H_2O$ (cf. *loc. cit.*); anhyd. salts give no colour, whilst an excess of $H_2O$ leads to yellow solutions. The colour varies from grey through blue and green to black, is roughly $\propto$ the increasing alkalinity of the salt [also shown by using solid buffers of $p_H$ (in solution) $> 10{\cdot}4$], and is given only by salts of acids having ionisation consts. $<$ that of (I) (primary stage). The reaction can be used to distinguish between, *e.g.*, $Na_3PO_4$ and $Na_2HPO_4$ (no colour), $Na_2CO_3$ and $NaHCO_3$ (no colour), (I) and *o*- or *m*-$C_6H_4(OH)_2$ (which do not show similar colour reactions), hydrated and anhyd. salts. H. B.

**Oxidation of quinol and of chloroquinol in presence of ammonium sulphite. Oxidation of a quinoldisulphonic acid in presence of ammonia.** (Mlle.) Y. Garreau (Compt. rend., 1936, **202**, 1186—1188).—Quinol or chloroquinol in dil. aq. $NH_3$ containing $(NH_4)_2S$, and $Cu(OH)_2$ afford α- (I) (cf. A., 1935, 338) and β-*diaminobenzoquinonedisulphonic acid* [$+2H_2O$; $(NH_4)_2$ salt$+3H_2O$, decomp. at 240°, which loses $1H_2O$ at 120°; $NH_4$ salt$+1H_2O$ (II)] either of which with warm KOH gives a K quinoldisulphonate. (II) affords ppts. with some bases of biological interest (cf. this vol., 337). J. L. D.

**New method of condensation.** C. Marschalk (Bull. Soc. chim., 1936, [v], **3**, 121—124).—Condensation of two mols. of a $C_6H_6$ or $C_{10}H_8$ derivative takes place in presence of $H_3BO_3$–$H_2SO_4$–anthraquinone-1 : 5- or -1 : 8-disulphonic acid, the H eliminated converting the latter into a leuco-derivative from which the sulphonic acid may be regenerated. In this way α-$C_{10}H_7{\cdot}OEt$ gives 4 : 4′-diethoxy-α-dinaphthyl (A., 1922, i, 1336), and 1 : 5-$C_{10}H_6(OH)_2$ yields a *compound*, readily oxidised by the air, insol. in boiling $H_2O$, sol. in alkalis, but which does not couple with diazotised *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$. The method is suitable for compounds sensitive to oxidising agents. H. G. M.

**Metabolism of polycyclic compounds. II. Production of dihydroxydihydroanthraceneglycuronic acid from anthracene.** E. Boyland and A. A. Levi (Biochem. J., 1936, **30**, 728—731).—The glycuronic acid compound (I) excreted when rabbits are fed a diet containing anthracene (A., 1936, 234), when warmed with dil. HCl gave *anthrylglycuronic acid* (II), $\alpha_D^{20}$ −52° in dioxan, *Na* salt, −79° (in water), which with boiling 0·2*N*-$H_2SO_4$ yielded a *compound*, probably α-anthrol (*Ac* derivative, m.p. 127°). Oxidation of (I) with $CrO_3$–AcOH and of (II) with alkaline $KMnO_4$ gave compounds, m.p. 185—186° and 193°, respectively, probably both 1-hydroxyanthraquinone. (I) with alkaline $KMnO_4$ gave 2 : 3-$C_{10}H_6(CO_2H)_2$. (I) is reduced with $H_2$ (Pd) to a *compound*, $C_{20}H_{22}O_8,2H_2O$, m.p. 188°, probably 1 : 2 - dihydroxy - 1 : 2 : 3 : 4 - tetrahydroanthraceneglycuronic acid, which with 2*N*-HCl yielded a *compound*, m.p. 149°, probably 2-keto-1 : 2 : 3 : 4-tetrahydroanthracene. Rats fed the same diet excrete much less glycuronic acid, but it is probable that they excrete an analogous lævorotatory compound which is readily hydrolysed to (II). It is concluded that (I) is 1 : 2-dihydroxy-1 : 2-dihydroanthracene-1-glycuronic acid. P. W. C.

**Action of thionyl chloride on *cyclo*hexanol.** P. Carré and D. Libermann (Bull. Soc. chim., 1936, [v], **3**, 144).—The dehydration of *cyclo*hexanol to *cyclo*hexene by $SOCl_2$, and the decomp. of *cyclo*hexyl sulphite when distilled under reduced pressure, are confirmed (cf. A., 1935, 480, 1492). H. G. M.

***cyclo*Hexylvinylcarbinol.** S. N. Danilov and S. M. Rizov (J. Gen. Chem. Russ., 1935, **5**, 1696—1698).—Mg *cyclo*hexyl bromide and acraldehyde in $Et_2O$ yield cyclo*hexylvinylcarbinol*, b.p. 89—91°/12 mm., the *acetate*, b.p. 94—103°/14 mm., of which was brominated, and the product treated with AgOAc in AcOH at 120°, to yield probably $C_6H_{11}{\cdot}CH(OAc){\cdot}CBr{:}CH_2$, b.p. 143—145°/2 mm. R. T.

**Mutual influence of radicals on their migration. Dehydration of phenyl*tert*.-amylcarbinol.** A. E. Favorski and P. A. Tichomolov (J. Gen. Chem. Russ., 1935, **5**, 1679—1684).—COPhPr, $NaNH_2$, and MeI afford *Ph* tert.-*amyl ketone*, b.p. 106—107°/8 mm., reduced by Na in EtOH to the corresponding *carbinol* (I), b.p. 124·5—125·5°/12—13 mm. (I) is converted by distillation from $KHSO_4$ into αβ-*dimethyl*-β-*ethylstyrene*, b.p. 99·5—100°/22·5 mm., 206·5—207°/764 mm., which yields COPhMe and COMeEt when ozonised. R. T.

**Manufacture of [triarylmethane] dyes.**—See B., 1936, 361.

***dl*-Tolylalanine and its bacterial decomposition.** T. Sasaki and I. Otsuka (J. Biochem. Japan, 1936, **23**, 139—146).—Glycine anhydride condensed with *o*-tolualdehyde (Sasuki, A., 1921, i, 196) yields 3 : 6 - *di* - (o - *methylbenzylidene*) - 2 : 5 - *diketopiperazine*, m.p. 273—274° [corresponding m-, m.p. 246—247° (decomp.), and p-*compounds*], reduced and hydrolysed to β-(o-*tolyl*)-α-*alanine*, m.p. 259—260° (decomp.) (*anhydride*, m.p. 228—230°) [corresponding *m*- (Böhm, A., 1914, i, 358) and *p*-compound (Dakin, A., 1911, ii, 416), and their *anhydrides*, m.p. 187—188° and 257—258°, respectively]. With *B. proteus*, only *p*-tolylalanine of the three isomerides yields β-(p-*tolyl*)-α-*lactic acid*, m.p. 79—80° (uncorr.), $[\alpha]_{\mathrm{Hg}}^{20}$ +27·82° (Na salt in $H_2O$). F. O. H.

**Complex formation between polynitro-compounds and aromatic hydrocarbons. II. The system 2 : 4-dinitro-2′-methyldiphenyl-6-carboxylic acid–benzene.** D. L. Hammick and R. B. Williams (J.C.S., 1935, 1856—1860).—*r*-2 : 4-Dinitro-2′-methyldiphenyl-6-carboxylic acid (I) [improved prep.; *monohydrate*, m.p. 120° (decomp.) on rapid heating; mono-MeOH *complex*, m.p. 130—135° (decomp.) on rapid heating] forms complexes with $C_6H_6$ in the molar ratios 2 : 1 and 1 : 1, m.p. about 138° and 128°, respectively (cf. A., 1930, 1287). (I) when resolved with brucine gives an active acid, $[\alpha]_{5791}$ −19·4° (cf. *loc. cit.*), but with *d*-α-phenylethylamine an acid (II), m.p. 135°, $[\alpha]_{5791}$ +89·1° in EtOH [d-α-*phenylethylamine* salt, m.p. 218°, $[\alpha]_{5791}$ +57·1° in $COMe_2$; *monohydrate*, m.p. 80—85° (decomp.), $[\alpha]_{5791}$ +84·6°; mono-MeOH *complex*, m.p. 90—100° (decomp.) on rapid heating], was obtained. The activity in EtOH of (II) is unchanged by complex formation with $H_2O$, MeOH, or $C_6H_6$ (cf. *loc. cit.*). Crystallisation of a mixture of (I) and (II) from $C_6H_6$ gives mother-liquors richer in (II), the $C_6H_6$ complex of (I) being sparingly sol. Only partial separation, however, can thus be obtained. Similarly 4 : 6 : 4′-trinitrodiphenic acid can be further resolved by crystallisation from $C_6H_6$. When resolved by quinine, the acid has $[\alpha]_{5461}$ −24·6° in $Et_2O$, but after recrystallisation from $C_6H_6$ the mother-liquors gave an acid of $[\alpha]_{5461}$ −42·2° in $Et_2O$. H. G. M.

**Apparent cases of liquid-crystal formation in *p*-alkoxybenzoic acids.** B. Jones (J.C.S., 1935, 1874).—The following p-*alkoxybenzoic acids*, prepared by refluxing *p*-OH·$C_6H_4$·$CO_2H$ with KOH–$H_2O$ and the appropriate alkyl iodide, melt sharply to milky liquids which at a higher temp. suddenly become clear. When the temp. is lowered 0·5—1·0° the clear liquid appears to become a mass of fine crystals (cf. A., 1930, 87). The transition point is given in parentheses. p-n-*Amyloxy*- (122°), m.p. 148°, p-n-*hexyloxy*- (105°), m.p. 150°, p-n-*heptyloxy*- (91°), m.p. 145°, p-n-*octyloxy*- (100°), m.p. 145°, p-*cetyloxy-benzoic acid* (99°), m.p. 131°. H. G. M.

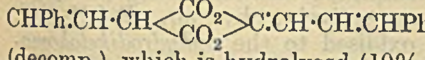
**Action of sulphuric acid on diarylphthalins. II. Mechanism of reaction.** F. F. Blicke and R. A. Patelski (J. Amer. Chem. Soc., 1936, **58**, 559—562).—The production of a 2 : 5-diaryl-3 : 4-benzfuran (I) from a diarylphthalin (II) and conc. $H_2SO_4$ is considered to occur thus: (II) is converted into ArH and an α-arylphthalide (by way of the benzhydrol-2-carboxylic acid), which then recombine to give either the 2-aroylbenzhydrol (III) or 2-hydroxy-2 : 5-diaryl-2 : 5-dihydro-3 : 4-benzfuran (IV); (III) or (IV) is then dehydrated to (I). This view is supported by the prep. of 2 : 5-dianisyl-3 : 4-benzfuran (V) from α-anisylphthalide (VI), PhOMe, and conc. $H_2SO_4$; (V) is oxidised ($Na_2Cr_2O_7$, AcOH–$H_2SO_4$) to 4′-methoxy-2-anisoylbenzophenone (VII). Similarly, (VI) and PhOH or α-*p*-hydroxyphenylphthalide (VIII) and PhOMe give 2-*p*-hydroxyphenyl-5-anisyl-3 : 4-benzfuran, converted by successive oxidation and methylation ($Me_2SO_4$, 10% NaOH) into (VII); (VIII) and PhOH afford 2 : 5-di-*p*-hydroxyphenyl-3 : 4-benzfuran, oxidised to 4′-hydroxy-2-*p*-hydroxybenzoylbenzophenone. Attempted prep. of compounds of type (III) results in the production of (I). Thus, *o*-CN·$C_6H_4$·CHO (IX) (p-*bromophenylhydrazone*, m.p. 194—195°), from *o*-CN·$C_6H_4$·$CHBr_2$ and $AgNO_3$ in 95% EtOH, with MgPhBr gives the *imine*, m.p. 126—127°, of 2-benzoylbenzhydrol; this is hydrolysed (HCl–$COMe_2$) to 2 : 5-diphenyl-3 : 4-benzfuran, oxidised to 2-benzoylbenzophenone. Similarly, the crude imine from (IX) and *p*-OMe·$C_6H_4$·MgI is hydrolysed to (V). 2-Benzylbenzophenone and MgPhBr afford 2-*benzyltriphenylcarbinol* (X), m.p. 133—134°, which is converted by cold conc. $H_2SO_4$ or hot AcOH into 9 : 9-diphenyl-9 : 10-dihydroanthracene. (X) is oxidised by dil. $HNO_3$ to 9 : 9-diphenyl-10-anthrone. H. B.

**Ester condensation and keten acetals. Existence of carbon monoxide acetals.** F. Adickes (Ber., 1936, **69**, [*B*], 654—656).—A reply to Scheibler (cf. this vol., 66), whose " phenylketen methyl benzoyl acetal " is probably *Me* β-*benzoyloxy*-αβ-*diphenylacrylate*. H. W.

**Action of nitrogen dioxide on tetraphenylsuccinonitrile.** G. Wittig and U. Pockels (Ber., 1936, **69**, [*B*], 790—792).—(·$CPh_2$·CN)$_2$ does not react with NO in boiling xylene alone or in presence of Cu powder or I. It is very readily converted by $NO_2$ in $CHCl_3$ into *nitrodiphenylacetonitrile* (I), m.p. 44—46°, the change affecting both radical and undissociated mol. Boiling, somewhat dil AcOH transforms (I) into *benzilonitrile* (II), m.p. 127—130° (decomp.), converted by alkali or boiling $H_2O$ into $COPh_2$ and HCN. (II) could not be obtained from $COPh_2$ and HCN in acid medium. LiPh and BzCN react very readily, but even at −60° the adduct passes into LiCN and $COPh_2$, transformed further into $CPh_3$·OH. H. W.

**Electrosynthesis of aromatic carboxylic acids. I. Electrolysis of opianic acid.** V. M. Rodionov, V. N. Belov, and V. V. Levtschenko (J. Gen. Chem. Russ., 1935, **5**, 1817—1829).—When K opianate is electrolysed with a constantly renewed Hg cathode, α-, m.p. 244—245°, and β-*dimeconyl*, m.p. 215°, are obtained; the compounds represent the racemic and meso-forms of dimeconyl. The α-isomeride is synthesised from opianyl chloride and Na–Hg in $C_6H_6$ at room temp. R. T.

**Carbon syntheses with malonic acid and related compounds. II. Aromatic aldehydes.** A. Michael and N. Weiner (J. Amer. Chem. Soc., 1936, **58**, 680—684; cf. A., 1933, 1142).—ArCHO cannot be condensed (using $Ac_2O$–conc. $H_2SO_4$; Meldrum, J.C.S., 1908, **93**, 605) with $CH_2(CO_2H)_2$, owing to the formation of $ArCH(OAc)_2$ and related inert compounds. Condensation occurs, however, with the mixed malonic acetic anhydride (I) of Ott (A., 1913, i, 1302). Thus, (I) and PhCHO give 81% of *α-carboxy-β-phenyl-β-propiolactone* (II), m.p. 148° (decomp.) (darkens at 135°), whilst methylmalonic acetic anhydride and PhCHO afford 75% of *α-carboxy-β-phenyl-α-methyl-β-propiolactone* (III), m.p. 176—178° (decomp.). $o\text{-}OH{\cdot}C_6H_4{\cdot}CHO$ and (I) give a little coumarin-3-carboxylic acid (IV), whilst $o\text{-}OAc{\cdot}C_6H_4{\cdot}CHO$ yields more (IV) and a little *o-acetoxybenzylidenemalonic acid*, m.p. 163° (decomp.). CHPh:CH·CHO (V) and (I) afford 30—35% of cinnamylidenemalonic acid (VI) and much tar; (V), $CH_2(CO_2H)_2$, and $Ac_2O$–conc. $H_2SO_4$ give (mainly) *cinnamylidene cinnamylidenemalonate* (VII),


$CHPh{:}CH{\cdot}CH{<}\genfrac{}{}{0pt}{}{CO_2}{CO_2}{>}C{:}CH{\cdot}CH{:}CHPh$, m.p. 157° (decomp.), which is hydrolysed (10% NaOH) to (VI), and with $NHPh{\cdot}NH_2$ affords CHPh:CH·CH:N·NHPh and (probably) the phenylhydrazide of (VI). (VII) is also obtained from (V), (VI), and $Ac_2O$–AcOH–conc. $H_2SO_4$. Contrary to Salkowski (A., 1924, i, 366), the production of $COMe_2$ by thermal decomp. of α-carboxy-β-*iso*butyrolactone and its α-Me derivative (VIII) is not due to the presence of the ββ-$Me_2$ groups; (II) decomposes at 160° to PhCHO and a little AcOH, whilst (III) gives (at 190°) PhCHO and a little $EtCO_2H$. PhCHO [with $CH_2(CO_2H)_2$ and $CHMe(CO_2H)_2$, respectively] is also formed by fission of (II) and (III) with 10% KOH at 100°; (VIII) similarly gives $COMe_2$ (cf. A., 1933 1142) whilst α-carboxy-ββ-pentamethylene-β-propiolactone affords *cyclo*hexanone [contrary to the result of Kandiah (A., 1932, 614)]. The above fissions thus involve the change $OH{\cdot}CR_2{\cdot}CR'(CO_2H)_2 \rightarrow COR_2 + CHR'(CO_2H)_2$. The formation (*loc. cit.*) of α-carboxy-α-methyl-β-butyrolactone from paracetaldehyde and $CHMe(CO_2H)_2$ is now considered not to be definitely established; the product obtained undergoes thermal decomp. to $CHMe(OAc)_2$ and $EtCO_2H$. The previously observed formation of α-methylbutyrolactone may be due to the production and recombination of MeCHO and CHMe:CO. H. B.

**Diphenyl series. IV. Action of oxalyl chloride on diphenyl derivatives.** N. Chatterjee (J. Indian Chem. Soc., 1935, **12**, 690—692).—4-*Methoxy-4′-methyldiphenyl*, m.p. 112° (obtained by methylation of the product formed from PhOH and a *p*-diazonium salt of toluene), when treated with $(COCl)_2$–$AlCl_3$–$CS_2$ at 0° gives 4-*hydroxy*-3 : 3′-*dicarboxy-4′-methyldiphenyl*, m.p. 280° (*Ac* derivative, m.p. 204°), which gives the $FeCl_3$ reaction for *o*-OH-acids and is oxidised by alkaline $KMnO_4$ to 4-methyl*iso*phthalic acid. 4-*Hydroxy*-3 : 4′-*dicarboxydiphenyl*, m.p. 304° (*Ac* derivative, m.p. 280°), and 2-*hydroxy*-5 : 4′-*dicarboxydiphenyl*, m.p. > 300° (*Ac* derivative, m.p. > 300°), which give, respectively, positive and negative $FeCl_3$ reactions and are oxidised to terephthalic acid, are similarly prepared. H. G. M.

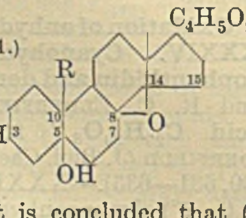
**Diphenic acid series. V. [Dipheneins.]** H. W. Underwood, jun., and G. Barker (J. Amer. Chem. Soc., 1936, **58**, 642—643).—Diphenic anhydride, *o*-cresol, and fuming $SnCl_4$ at 125—135° give o-*cresoldiphenein*, m.p. 218·5—219·5° [$Br_2$-, m.p. 203—204°, $I_2$-, m.p. 206—207°, and $(NO_2)_2$-, m.p. 212·5—213°, derivatives]. The $Br_4$-, m.p. 213—214°, $I_2$-, m.p. 216—217°, and $(NO_2)_2$-, m.p. 212·5—213°, derivatives of phenoldiphenein (I) (A., 1924, i, 176, 1197) are also described. All the known substitution products of (I) dissolve in dil. NaOH to pale yellow solutions. H. B.

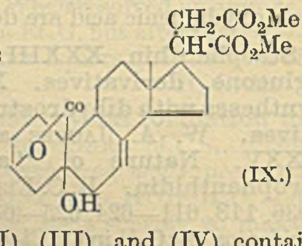
**Absorption spectra of dipheneins.** H. W. Underwood, jun., L. Harris, and G. Barker (J. Amer. Chem. Soc., 1936, **58**, 643—645).—The absorption spectra of phenol- (I), *o*-cresol- (II), and resorcinol- (III) -dipheneins in EtOH show a band of high extinction coeff. at 2950 A.; the effect of halogen substitution is discussed. (I), (II), (III), and tetrabromophenoldiphenein in EtOH–KOH show a strong absorption band at 3550 A.; the original configurations have undergone a marked change. All the spectra are different from those of the phthaleins. H. B.

**Relative rates of racemisation of substituted diamides of 6 : 6′-dimethoxydiphenic acid. XLII.** C. Y. Hsing and R. Adams (J. Amer. Chem. Soc., 1936, **58**, 587—589).—The *methylamide* (I), m.p. 268—270° (all m.p. are corr.), $[\alpha]_D^{20}$ −88·9° in MeOH, *ethylamide* (II), m.p. 233°, $[\alpha]_D^{20}$ −84·7° in MeOH, *dimethylamide* (III), m.p. 133°, $[\alpha]_D^{20}$ −93·5° in MeOH, and *diethylamide* (IV), m.p. 125—126°, $[\alpha]_D^{20}$ −86·5° in MeOH, of *l*-6 : 6′-dimethoxydiphenic acid (V) (A., 1933, 392) are obtained from the chloride [from (V) and $SOCl_2$ at room temp.] and the appropriate base. The rates of racemisation in boiling AcOH are in the order: amide (*loc. cit.*) and (III)>(IV)>(I)>(II). The *hydrazide*, m.p. 263—265°, $[\alpha]_D^{20}$ −50·67° in AcOH, of (V) is first acetylated; racemisation then occurs at a rate < (III) but > (IV). The *dimethylamide*, m.p. 175—176°, and *hydrazide*, m.p. 254—255° ($Ac_2$ derivative, m.p. 284—286°), of *dl*-6 : 6′-dimethoxydiphenic acid are described. H. B.

**Strophanthin. XXXIII. Oxidation of anhydroaglucone derivatives. XXXIV. Cyanohydrin syntheses with dihydrostrophanthidin and derivatives.** W. A. Jacobs and R. C. Elderfield. **XXXV. Nature of "acid $C_{23}H_{30}O_8$" from strophanthidin.** R. C. Elderfield (J. Biol. Chem., 1936, **113**, 611—624, 625—630, 631—635).—XXXIII. Oxidation ($BzO_2H$ in $CHCl_3$ at 0—5°) of monoanhydrodihydrostrophanthidin (I) gives an *oxide* (II) (*A*, R=CHO), m.p. 248°, which still contains CHO since it yields an *oxime*, m.p. 258—260° (previous softening). *Monoanhydrodihydroperiplogenin* (III), m.p. 230—234° (previous softening) [from dihydroperiplogenin and HCl (*d* 1·1) in MeOH], similarly affords an *oxide*, m.p. 252—258°, $[\alpha]_D^{20}$ +54° in $C_5H_5N$ (also formed by oxidation with $KMnO_4$ in aq. AcOH), and monoanhydrodihydrodigitoxigenin (IV) gives an *oxide*, m.p. 215° (variable; softens at 205—210°); non-cryst. products were obtained on attempted fission of the ·O· ring. Oxidation ($KMnO_4$, $COMe_2$) of (II) affords *oxidomonoanhydrodihydrostrophanthidinic acid* (*A*, $R=CO_2H$), m.p. 252—254° (decomp.) (softens about 212°) [also obtained from (I) and 5% $KMnO_4$ in AcOH (cf. A., 1935, 497)] [*Me* ester (V), m.p. 229—243°, $[\alpha]_D^{26}$ +59° in $C_5H_5N$], which is converted (by hydration of the ·O· ring and subsequent loss of $2H_2O$) by 50% AcOH at 100° into an *anhydrodilactone* (VI), $C_{23}H_{30}O_6$, m.p. 260—284°, $[\alpha]_D^{24}$ +98° in $C_5H_5N$ [(3-)*benzoate*, m.p. 265°; (5-)*sulphite*, m.p. 242—243°, obtained using $SOCl_2$ at 0°]. (VI) is also obtained from (II) and 0·1*N*-NaOH followed by 5% $KMnO_4$ in $C_5H_5N$. Oxidation (Kiliani's $CrO_3$ solution; 90% AcOH) of (VI) gives a *ketoanhydrodilactone*, $C_{23}H_{28}O_6$, m.p. 251°, thus showing the presence of $C_{(3)}H·OH$; catalytic reduction results in the uptake of 1 mol. of $H_2$. (VI) thus appears to contain the $\Delta^{14:15}$ (or $\Delta^{7:8}$) double linking and the $C_{(10)}·CO·O·C_{(8)}$ (or $C_{(10)}·CO·O·C_{(14)}$) group. (V) and 50% AcOH at 100° followed by a little 5% $H_2SO_4$, give (by fission of ·O· ring and then loss of $2H_2O$) a *dianhydrolactone Me* ester, $C_{24}H_{32}O_6$, m.p. 199° (softens about 190°), which probably contains $C_{(10)}·CO_2Me$ and the $\Delta^{7:8}$ and $\Delta^{14:15}$ double linkings. Reduction ($H_2$, $PtO_2$, EtOH) of (II) furnishes the *trihydroxylactone oxide* (*A*, R=$CH_2·OH$), m.p. 265°, $[\alpha]_D^{28}$ +47° in $C_5H_5N$ [*dibenzoate* (VII), softens about 145—150° and then melts slowly], converted by hot 50% AcOH into an isomeric *trihydroxylactone oxide* (VIII), m.p. 282° (decomp.), $[\alpha]_D^{28}$ +83° in $C_5H_5N$ (*benzoate*, m.p. 274—275°), which is oxidised ($CrO_3$, 90% AcOH) to a *ketodihydroxylactone oxide*, $C_{23}H_{32}O_6$, m.p. 272° (decomp.) (softens about 260°). (VIII) thus appears to contain OH groups at $C_{(3)}$, $C_{(5)}$, and $C_{(14)}$ (or $C_{(8)}$) and the $C_{(10)}·CH_2·O·C_{(8)}$ (or $C_{(10)}·CH_2·O·C_{(14)}$) group. (VII) and 75% AcOH–10% $H_2SO_4$ give, however, the *dibenzoate*, m.p. 210—211°, of a pentahydroxylactone, *i.e.*, $C_{(3)}·OBz$, $C_{(10)}·CH_2·OBz$, and OH at $C_{(5)}$, $C_{(8)}$, and $C_{(14)}$. Oxidation ($BzO_2H$ or $KMnO_4$–AcOH) of $Me_2$ anhydro-β-*iso*strophanthic lactone acid ester (A., 1929, 1456) also affords an *oxide*, m.p. 244—245° (softens at 240°), $[\alpha]_D^{20}$ −26° in $C_5H_5N$, converted by 50% AcOH–10% $H_2SO_4$ into the *dianhydrolactone $Me_2$* ester (IX), m.p. 178—180°.

(*A*.)

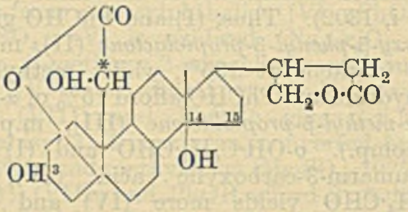




(IX.)

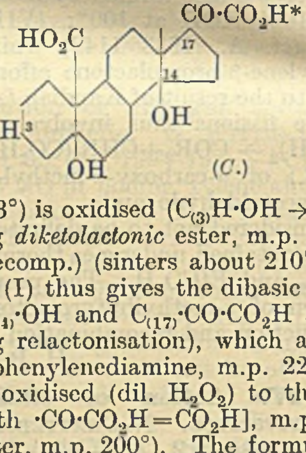
It is concluded that (I), (III), and (IV) contain either the $\Delta^{14:15}$ or $\Delta^{8:14}$ double linking; the former may predominate in alkaline, the latter in neutral and acid, solution; alternatively, both forms may occur simultaneously but oxidation proceed at different rates. The β-anhydrodigitoxigenin (X) of Smith (A., 1935, 1226) can be converted into the α-isomeride (XI) by conc. acid. Dehydration of digitoxigenin may thus give (X) and then (by isomerisation) (XI). The change (X) → (XI) may, however, involve merely a shift of the double linking.

XXXIV. Dihydrostrophanthidin with KCN and $NH_4Cl$ in aq. EtOH gives a cyanohydrin (not isolated), hydrolysed (hot aq. AcOH) to α-, m.p. 254° (decomp.), $[\alpha]_D^{25}$ −36° in $C_5H_5N$ [*benzoate* (I), m.p. 320°], and β-, m.p. 235° (decomp.) (softens about 175°), $[\alpha]_D^{25}$ +30° in $C_5H_5N$, *homodilactones* [as (*B*)], the isomerism being due to the creation of a new centre of asymmetry at C*. These are both oxidised (Kiliani's $CrO_3$ solution; 90% AcOH) to the *diketohomodilactone* [(*B*) with $C_{(3)}H·OH$ and C*H·OH both=CO], m.p. 189—190° (decomp.), $[\alpha]_D^{27}$ +75° in $C_5H_5N$, and are dehydrated (loss of $H_2O$ between $C_{(14)}$ and $C_{(15)}$) to α- (II), m.p. 302—303°, $[\alpha]_D^{21}$ −72° in $C_5H_5N$, and β-, m.p. 305° (decomp.) (previous softening), *-anhydrohomodilactones*, respectively, by aq. EtOH–HCl. (II) is similarly oxidised to the *anhydrodiketohomolactone*, m.p. 196° (decomp.) (softens about 191°). Dihydrostrophanthidin benzoate with KCN and $NH_4Cl$ in aq. $C_5H_5N$ affords a *cyanohydrin*, m.p. 258° (decomp.), hydrolysed (repeated evaporation with 50% AcOH) to a *homodilactone benzoate*, m.p. 305—306° (decomp.) [isomeric with (I)], dehydrated to the *anhydrohomodilactone benzoate*, m.p. 265—268° (slight previous softening), $[\alpha]_D^{26}$ −38° in $C_5H_5N$.



(*B*.)

XXXV. The acid, $C_{23}H_{30}O_8$, previously obtained (A., 1924, i, 65) by successive alkaline hydrolysis and oxidation ($KMnO_4$) of strophanthidinic acid, is now shown to be a monobasic lactonic acid, $C_{21}H_{28}O_7$ (*I*) [(*C*) with lactone group between $C_{(14)}·OH$ and $CO_2H$*]; its Me, ester (cf. *loc. cit.*) (p-*bromophenylhydrazone*, m.p. 273°) is oxidised ($C_{(3)}H·OH$ → CO) to the corresponding *diketolactonic* ester, m.p. 228° [*dioxime*, m.p. 233° (decomp.) (sinters about 210°)]. Alkaline hydrolysis of (I) thus gives the dibasic keto-acid (*C*) (in which $C_{(14)}·OH$ and $C_{(17)}·CO·CO_2H$ are *trans*, thus preventing relactonisation), which affords a *compound* with *o*-phenylenediamine, m.p. 222—224° (decomp.), and is oxidised (dil. $H_2O_2$) to the *dicarboxylic acid* [(*C*) with $·CO·CO_2H=CO_2H$], m.p. 295° (decomp.) (*$Me_2$* ester, m.p. 200°). The formulæ for other derivatives (*loc. cit.*) of (I) are revised. H. B.



(*C*.)

**Synthesis of conjugated bile acids. II. Glycodeoxycholic acid.** F. CORTESE and L. BAUMAN (J. Biol. Chem., 1936, **113**, 779—785).—The unstable *chloride*, m.p. 104° (corr.; slight decomp.), of diformyldeoxycholic acid (I) with conc. aq. $NH_3$ and a little conc. aq. NaOH gives deoxycholamide, m.p. 188—189° (corr.) (softens about 162°). Glycodeoxycholic acid (+$H_2O$) (II) [prep. essentially by procedure described (A., 1935, 1237) for glycocholic acid] appears to exist in normal, m.p. 107°, and para, m.p. 186—187° (corr.), forms. (II) forms mixed crystals with small amounts of stearic (III) and the choleic acids from (III) and oleic acid. The "glycocholeic acids" of Wahlgren (A., 1903, i, 302) and Sekitoo (A., 1931, 1179) are mixtures of (II) and a small amount of fatty acid; xyleneglycocholeic acid

(Sekitoo, *loc. cit.*) is probably impure (II). Et deoxycholate, (I), and (II) do not form co-ordination compounds with (III); free OH and $CO_2H$ groups thus appear necessary (as in deoxycholic acid) for such reaction. The so-called "choleic acid principle" (Wieland and Sorge, A., 1916, i, 710) appears to be of no practical importance either in digestion or in the transport of cholesterol in bile. H. B.

**Synthesis of *cyclo*hexane-1 : 1 : 4 : 4-tetracarboxylic and -1 : 4-dicarboxylic acids.** V. V. Feolaktikov and A. A. Ivanov (J. Gen. Chem. Russ., 1935, 5, 1558—1561).—$Mg[CH(CO_2Et)_2]_2$ and $C_2H_4Br_2$ in EtOH yield $Et_4$ *cyclo*hexane-1 : 1 : 4 : 4-tetracarboxylate, m.p. 75·5—76·5°, converted by alkaline hydrolysis into the free acid, which decomposes at 240° to yield *cis-trans-cyclo*hexane-1 : 4-dicarboxylic acid. R. T.

**Hydrogen cyanide. VII. Aldehydes from aromatic hydrocarbons.** L. E. Hinkel, E. E. Ayling, and J. H. Beynon (J.C.S., 1936, 339—346).—The application of the HCN synthesis of aromatic aldehydes has been extended to substituted benzenes and to polynuclear hydrocarbons. By the introduction of suitable liquid reaction media, such as $C_2H_2Cl_4$, PhCl, and $o$-$C_6H_4Cl_2$, it has been possible to extend the synthesis to solid hydrocarbons and to facilitate the complete conversion of hydrocarbon into aldehyde. The influence of the solvent on the reaction, with reference to the secondary action of the $AlCl_3$ on the hydrocarbon and the temp. and reaction period, is discussed. $C_2H_2Cl_4$ appears to enhance the aldehyde synthesis with most hydrocarbons, but with certain hydrocarbons it increases the tendency to polymerisation.

The following have been prepared: 1 : 6-*dimethyl-4-naphthaldehyde*, b.p. 191·5°/16 mm. (*oxime*, m.p. 123°; *semicarbazone*, m.p. 202°; *phenylhydrazone*, m.p. 110°); 2 : 6-*dimethyl-1-naphthaldehyde*, m.p. 57° (*oxime*, m.p. 122—123°; *semicarbazone*, m.p. 214°; *phenylhydrazone*, m.p. 122°; $NH_2Ph$ *derivative*, m.p. 78°); *anthracene-9-aldehyde*, m.p. 104—105° ($NH_2Ph$ *derivative*, m.p. 175°; *phenylhydrazone*, m.p. 207°; *oxime*, m.p. 186—187°; *semicarbazone*, m.p. 291°); *acenaphthene-3-aldehyde*, m.p. 87° (*phenylhydrazone*, m.p. 140°; 2 : 4-*dinitrophenylhydrazone*, m.p. 273°; *oxime*, m.p. 126·5°; *semicarbazone*, m.p. 234°; $NH_2Ph$ *derivative*, m.p. 97°); *fluorene-2-aldehyde*, m.p. 90° ($NH_2Ph$ *derivative*, m.p. 158°; *phenylhydrazone*, m.p. 202—203°; *oxime*, m.p. 156—157°; *semicarbazone*, m.p. 278°). The prep. of the aldehydes by the substitution of chloromethyleneformamidine for HCN and HCl has been extended to acenaphthene, anthracene, hydrindene, and $C_{10}H_8$; but with $Ph_2$ in PhCl, diphenyl-4-aldehyde, and in $C_2H_2Cl_4$, diphenyl-4 : 4′-dialdehyde are obtained. F. R. S.

**Action of mixed organo-magnesium derivatives on benzaldehydesemicarbazone.** (Mlle.) D. Biquard (Bull. Soc. chim., 1936, 3, [v], 666—668).—The action of MgEtBr on $CHPh:N\cdot NH\cdot CO\cdot NH_2$ (I) establishes the presence of 3 active H and leads to COPhEt and $EtCO\cdot NH_2$. Similarly (I) and MgBuCl afford COPhBu and $BuCO\cdot NH_2$. The possible intermediate formation of $CO(NH_2)_2$ is negatived by the non-formation of the amides from this source, whilst the products from $NH_2\cdot CO\cdot NHPh$ are quite different from those from (I). The suggested mechanism is therefore

$$CHPh:N\cdot NH\cdot CO\cdot N(MgX)_2 + 2MgRX \rightarrow$$
$$CHPhR\cdot N(MgX)\cdot N(MgX)\cdot CO\cdot N(MgX)_2 \rightarrow$$
$$(+H_2O)\ CPhR:NH + NH_3 + R\cdot CO\cdot NH_2.$$

H. W.

**Formation of half-acetals of aldehydes, $CH_2R\cdot CHO$. Nature of their solution in benzyl alcohol. II. Constitution of phenyl- and $p$-tolyl-acetaldehyde and hydratropaldehyde on the basis of their electron distribution.** A. Müller (Helv. Chim. Acta, 1936, 19, 225—234; cf. A., 1934, 1301).—When $CH_2Ph\cdot OH$ (I) is mixed with $p$-$C_6H_4Me\cdot CH_2\cdot CHO$ (II), $CH_2Ph\cdot CHO$ (III), or $CHPhMe\cdot CHO$ (IV), gradual evolution of heat and change in $\eta$, capillariscopic behaviour, and $n$ occur. Enolisation is involved in the change, since the mixture of (I) and (III) does not immediately absorb acid-free Br in $CCl_4$; after some time rapid absorption occurs. The relative amounts of the changes in physical consts. show that the order of reactivity is (III)>(II)≫(IV). Compound formation is proved by isolation of an unstable 1 : 1-additive *compound* of (I) and (II), m.p. 61·62° after sintering at 58°, formulated as $p$-$C_6H_4Me\cdot CH:CH\cdot OH \cdots CH_2Ph\cdot OH$, but no such product could be obtained from (III) or (IV). The above phenomena, allied to electronic considerations which are in line with the relative reactivities, confirm the previously (*loc. cit.*) propounded mechanism: $CH_2R\cdot CHO + R'\cdot OH \rightarrow CH_2R\cdot CHO \cdots R'\cdot OH \rightarrow CHR:CH\cdot OH \cdots R'\cdot OH \rightarrow CH_2R\cdot CH(OH)\cdot OR'$. R. S. C.

**Cannizzaro reaction. IV. Halogeno-derivatives of $m$-hydroxybenzaldehyde.** G. Lock [with G. Nottes] (Monatsh., 1936, 67, 320—327; cf. A., 1935, 1238).—Treatment of $m$-$OH\cdot C_6H_4\cdot CHO$ with $Cl_2$ in AcOH at 100° and of the crude product with $SnCl_2$ in conc. HCl gives 3 : 2 : 4 : 5 : 6-$OH\cdot C_6Cl_4\cdot CHO$, m.p. 197—198°, in 88·5% yield; it is converted by 50% KOH at 100° into 2 : 3 : 4 : 6-$C_6HCl_4\cdot OH$ and $HCO_2K$. 3 : 2 : 4 : 5 : 6-$OEt\cdot C_6Cl_4\cdot CHO$, m.p. 68·5°, similarly gives 2 : 3 : 4 : 6-$C_6HCl_4\cdot OEt$ and $HCO_2K$. 3 : 6-$OH\cdot C_6H_3Br\cdot CHO$ (I) and $Cl_2$ in AcOH at 40—50° give 2-*chloro-6-bromo-3-hydroxybenzaldehyde*, m.p. 137° (corr.) (*Et ether*, m.p. 87°; *phenylhydrazone*, m.p. 107°), transformed by 50% KOH at 100° into 2 : 4-$C_6H_3ClBr\cdot OH$ and $HCO_2K$. Further chlorination of (I) affords 2 : 4-*dichloro-6-bromo-3-hydroxybenzaldehyde*, m.p. 111° [*Et ether*, m.p. 73°; *oxime*, m.p. 181° (corr.)], which yields 2 : 6 : 4-$C_6H_2Cl_2Br\cdot OH$ and $HCO_2K$. 3 : 2-$OH\cdot C_6H_3I\cdot CHO$ and 50% KOH at 100° give 2-*iodo-3-hydroxybenzyl alcohol*, m.p. 154° (corr.), and 3 : 2-$OH\cdot C_6H_3I\cdot CO_2H$. 4 : 6-*Dibromo-2-iodo-3-hydroxybenzaldehyde*, m.p. 133·5° (corr.) (*oxime*, m.p. 168°), gives 4 : 6 : 2-$C_6H_2Br_2I\cdot OH$. H. W.

**Preparation of aldehydes from nitriles (Stephen's method). $\gamma$-Phthalimidobutaldehyde.** F. E. King, P. L'Ecuyer, and (in part) H. T. Openshaw (J.C.S., 1936, 352—354).—The modification recently introduced into Stephen's method for the prep. of aldehydes from nitriles (A., 1934, 89) has been applied to the prep. of $\alpha$-$C_{10}H_7\cdot CHO$

(2 : 4-*dinitrophenylhydrazone*) and *o*-$C_6H_4$Me·CHO (2 : 4-*dinitrophenylhydrazone*, m.p. 193—194°), for which the original process is unsatisfactory, but without any marked improvement. γ-*Phthalimidobutaldehyde* (2 : 4-*dinitrophenylhydrazone*, m.p. 184°) is prepared from the nitrile and $SnCl_2$–HCl. F. R. S.

**Preparation of acenaphthylene glycol and some condensation reactions of naphthalene-1 : 8-dialdehyde.** B. K. Blount and A. Weissberger (J.C.S., 1936, 336—337).—Reduction of acenaphthenequinone with Na–Hg and EtOH in $N_2$ gives *cis*-acenaphthylene glycol, oxidised to 1 : 8-$C_{10}H_6(CHO)_2$, which condenses with acetonedicarboxylic acid and $MeNH_2$ to 1-methyl-2 : 6(1′ : 8′)-naphthapiperid-4-one, isolated as the *picrate*, m.p. 197°, and the *picrate*, m.p. 165—166°, of a base, $C_{13}H_{13}N$. F. R. S.

**Beckmann rearrangement of 2-alkyl-*cyclo*pentanone- and -*cyclo*hexanone-oximes.** J. G. Hildebrand, jun., and M. T. Bobert (J. Amer. Chem. Soc., 1936, 58, 650—652).—*Et* 2-*propyl*cyclo*pentanone*-2-*carboxylate*, b.p. 136·5—138°/28 mm. (*semicarbazone*, m.p. 160—161°), prepared by propylation of Et *cyclo*pentanone-2-carboxylate (improved prep.), is hydrolysed (conc. HCl) to 2-propyl*cyclo*pentanone [*oxime* (I), b.p. 120—121·5°/13 mm.]. 2-Methyl- and 2-ethyl-*cyclo*pentanoneoximes and (I) are converted by hot 75—80% $H_2SO_4$ into 6-methyl-, 6-*ethyl*-, m.p. 88·5—89·6° (corr.), and 6-*propyl*- (II), m.p. 91·5—92·4°, -2-*piperidone*, respectively (59—76% yield); none of the 3-alkyl-2-piperidone is produced. 2-Methyl*cyclo*hexanoneoxime and 96·4% $H_2SO_4$ give 97% of the *lactam*, m.p. 90·5—91·5° (cf. Wallach, A., 1906, i, 514), of ε-*aminoheptoic acid*, m.p. 196—197·5° (corr.), which is deaminated (98% HI) to *n*-$C_6H_{13}$·$CO_2H$. (II) is also obtained when homoconic (δ-amino-octoic) acid (Baum, A., 1886, 562) is heated at 165°. H. B.

**Behaviour of keten in the Friedel–Crafts reaction.** F. S. Spring and T. Vickerstaff (J.C.S., 1935, 1873—1874).—Keten (cf. A., 1934, 1091) when passed at 0° into $C_6H_6$–$AlCl_3$ gives COPhMe and some *p*-$C_6H_4$Et·COMe (*semicarbazone*, m.p. 196°); the latter is considered to be due to the presence of $C_2H_4$ in keten. PhOH when treated with keten at 80° gives its Ac derivative (cf. *loc. cit.*). H. G. M.

**Influence of cyclisation on the "colour" of molecules. Ultra-violet absorption of derivatives of diphenylmethane and fluorene.** (Mme.) Ramart-Lucas and M. J. Hoch (Bull. Soc. chim., 1935, [v], 2, 1376—1380).—Comparison of the ultraviolet absorption spectra of $CH_2Ph_2$, $CHPh_3$, $CMePh_2$·OH, $CPh_2$:CHMe, $COPh_2$, and $CPh_2$:N·OH in EtOH or $C_6H_{12}$ with the spectra of, respectively, fluorene (I), 9-phenylfluorene, 9-hydroxy-9-ethylfluorene, 9-ethylidenefluorene, fluorenone (*semicarbazone*, m.p. 245°), and its oxime, shows that an *o*-linking between the two Ph in $CH_2Ph_2$ causes a large displacement of absorption towards the visible and an alteration in the form of the absorption curves. The absorption spectra of (I) in the lit. show fine bands which are due to an impurity. J. W. B.

**Walden inversion. XIII. Configurative relationship between optically active desylamine and benzoin.** A. McKenzie and D. J. C. Pirie (Ber., 1936, 69, [*B*], 876—879).—(−)-Benzoin and (+)-desylamine have the same configuration. Reduction of desylamine hydrochloride by Na–Hg in EtOH–AcOH affords *r*-β-hydroxy-αβ-diphenylethylamine (I), m.p. 164° (identical with the product from β-benzilmonoxime), and a trace of the *iso*-compound, m.p. 130°; reduction in presence of Pt gives (I) exclusively. (−)-Desylamine hydrochloride gives (+)-β-hydroxy-αβ-diphenylethylamine, m.p. 141—143°, $[\alpha]_D$ +10·4° in EtOH. (−)-Benzoin-α-oxime affords (−)-β-hydroxy-αβ-diphenylethylamine, m.p. 141—142°, $[\alpha]_D$ −10° in EtOH, also obtained from the corresponding β-oxime. H. W.

**Retene. V. Structure of 6-acetylretene.** D. E. Adelson and M. T. Bogert (J. Amer. Chem. Soc., 1936, 58, 653—654).—The acetylretene (I), m.p. 99·5—100° (corr.), obtained by a slight modification of the method previously used (A., 1931, 1297) is the 6-derivative, since its oxime is converted by $PCl_5$ in $Et_2O$ into the *Ac* derivative, m.p. 240—240·5° (corr.) (decomp.), of 6-*aminoretene* (II), m.p. 139·5—140° (corr.). (II) is converted (diazo-method) into 6-retenol. Retene-6-carboxylic acid is conveniently prepared from (I) and I–KI in dioxan-10% NaOH. H. B.

**Uneven halides. II. Uneven halides of the benzanthrone series.** K. Brass and E. Clar (Ber., 1936, 69, [*B*], 690—692).—Benzanthrone unites with Br and I in the ratio 1 : 1 giving dark, moderately stable *compounds*. With excess of I compounds of indefinite stoicheiometric composition are obtained which lose the excess of halogen when warmed in vac. and give the compound with ratio 1 : 1. 1-Bromobenzanthrone combines with Br and I in the ratios 2 : 1 and 3 : 2, respectively. All the substances yield the halogen quantitatively to mild reducing agents and pass into the initial materials. The observations confirm the conclusion that the trihalides of perylene (A., 1933, 57) have the composition $C_{20}H_{12}Br+Br_2$ and $C_{20}H_{12}I+I_2$, respectively. H. W.

**Novel ring systems. II. 1 : 8-Naphthaloylnaphthalene.** W. Knapp (Monatsh., 1936, 67, 332—343).—1 : 8-$C_{10}H_6(CO)_2O$ is converted by MgPhBr in $Et_2O$ into 8-*benzoyl*-1-*naphthoic acid*, m.p. 129—130°, which is scarcely affected by warm, conc. $H_2SO_4$, $P_2O_5$ in PhMe, or $AlCl_3$–NaCl at 130°. 8-1′-Naphthoyl-1-naphthoic acid and $P_2O_5$ in boiling PhMe afford 1 : 8-*naphthaloylnaphthalene* (I), m.p. about 350° (incipient decomp.), in about 10% yield, also obtained by use of $AlCl_3$–NaCl at 140° or of conc. $H_2SO_4$ at 150°. (I) dissolves in conc. NaOH with production of a *Na* salt. The Mg derivative of 1 : 2-$C_{10}H_6$Br·OMe, m.p. 83—84° (prep. from β-$C_{10}H_7$·OMe and Br in AcOH described), and 1 : 8-$C_{10}H_6(CO)_2O$ give 8-2-*methoxynaphthoylnaphthoic acid*, m.p. 215—217°, converted by $P_2O_5$ in boiling PhMe into 2-*methoxy*-1 : 8-*naphthaloylnaphthalene* (II), m.p. about 370° (*Na* salt). 1 : 8-$C_{10}H_6(CO)_2O$, β-$C_{10}H_7$·OH, and $AlCl_3$ at 200—210° yield 2-*hydroxy*-1 : 8-*naphthaloylnaphthalene*, m.p. about 360° (decomp.) (*Na* salt), transformed with difficulty by

$Me_2SO_4$ into (II). 1 : 8-$C_{10}H_6(COCl)_2$, β-$C_{10}H_7$·OMe, and $AlCl_3$ in boiling $C_2H_2Cl_4$ give a *product* $C_{22}H_{12}O_3$, m.p. about 340°, which yields very small amounts of a hydrocarbon, m.p. 155—158°, when distilled with Zn dust. H. W.

**Formation of *s*-dibenzo*cyclo*docosanedione.** M. Uenaka and B. Kubota (Bull. Chem. Soc. Japan, 1936, **11**, 19—26).—*o*-Phenylenediacrylic acid is obtained together with some phthalyl alcohol $Et_2$ ether and o-*ethoxymethylcinnamic acid*, m.p. 130—130·5° (corr.) [*Et* ester, b.p. 140—141°/2 mm.; *dibromide*, m.p. 168—169° (corr.); *dihydro*-derivative, m.p. 85°], from *o*-$C_6H_4(CH_2Br)_2$, $CClNa(CO_2Et)_2$ (containing some $Cl_2$-ester), and KOH–EtOH, and is reduced (Na–Hg) to *o*-phenylenedipropionic acid (I). The formation of some β-(*o*-ethylphenyl)propionic acid was also observed. The $Et_2$ ester of (I) is reduced (Na–EtOH) to o-*phenylenedipropyl alcohol*, m.p. 56—57° (p-*xenylcarbamate*, m.p. 187°), converted by HBr into the *dibromide*, b.p. 187—189°/7·5 mm., which on malonation and subsequent hydrolysis and heating gives o-*phenylenedivaleric acid*, m.p. 148—149° (corr.). The *Th* salt of this acid, when heated at 0·008—0·009 mm. pressure, gives s-*dibenzo*cyclo-*docosanedione*, m.p. 133·5° (corr.) [*semicarbazone*, decomp. 205—208° (corr.); p-*nitrophenylhydrazone*, m.p. 168—172°]. An 11-membered ring-monoketone was not formed. H. G. M.

**Preparation of βγ-Δ⁵-unsaturated ketones of the sterol series. 17-Ethyltestosterone.** A. Butenandt and J. Schmidt-Thomé (Ber., 1936, **69**, [*B*], 882—888).—βγ-$\Delta^5$-Unsaturated ketones of the sterol group are readily obtained when 5 : 6-dibromoketones are debrominated by short treatment with Zn dust in warm MeOH or EtOH; under these conditions displacement of the double linking is not observed. Thus, cholesterone dibromide is transformed into $\Delta^5$-*cholestenone* (I), m.p. 127° after softening (? partial isomerisation to the $\Delta^4$-compound), $[\alpha]_D^{20}$ −4·2° in $CHCl_3$ [*oxime*, m.p. 188° (decomp.)]. Analogously, dehydroandrosterone is brominated at the double linking and debrominated by Zn dust in MeOH after oxidation of OH to $\Delta^5$-*androstene*-3 : 17-*dione*, m.p. 158° after softening at 140° (*dioxime*, m.p. about 205° after incipient decomp. at 180°). The constitution of the ketones is established by the observations that (I) yields a dibromide identical with that obtained by the oxidation of cholesterol dibromide and that debromination of the latter with Zn dust and MeOH affords cholesterol. The βγ-$\Delta^5$-unsaturated ketones are readily isomerised to the $\Delta^4$-compounds when heated in dil. (mineral) acidic or alkaline solution. In neutral solvents they can be crystallised unchanged. αβ-Unsaturated ketones can be obtained from the 5 : 6-dibromides by feebly acidic MeOH or EtOH in place of the usual AcOH. 17-Ethyl-$\Delta^5$-androsten-17-ol-3-one (previously regarded as the $\Delta^4$-compound) is converted by short warming with EtOH containing a little $H_2SO_4$ into the isomeric 17-*ethyltestosterone*, m.p. 139° [*semicarbazone*, m.p. 230° (decomp.)], also obtained directly from 17-ethylandrostenediol by successive bromination, oxidation, and debromination by Zn dust in MeOH–$H_2SO_4$. When distilled in a high vac. it gives the doubly unsaturated *ketone*, $C_{21}H_{30}O$, m.p. 135° [*semicarbazone*, m.p. about 225° (decomp.)]. H. W.

**Δ⁵-Pregnene-3 : 20-dione, an isomeride of progesterone.** U. Westphal and J. Schmidt-Thomé (Ber., 1936, **69**, [*B*], 889—892).—$\Delta^5$-Pregnen-3-ol-2-one is brominated (=2Br) in AcOH and then oxidised with $CrO_3$; the product is debrominated by Zn dust in MeOH to $\Delta^5$-*pregnene*-3 : 20-*dione* (I), m.p. 158—160°, $[\alpha]_D^{20}$ +65·5° in $CHCl_3$ [*dioxime*, m.p. 203—205° (darkening), complete decomp. 207°]. (I) is so readily transformed by $H_2SO_4$–EtOH into α- and β-progesterone that the process can be followed polarimetrically. After being heated above its m.p. in a glass tube (I) shows an increase in [α], probably due to partial wandering of the double linking. H. W.

**Chelation. IV. Some properties of 2 : 3-dihydroxyphenyl ketones.** W. Baker and A. R. Smith (J.C.S., 1936, 346—348).—The volatility and solubility of 2 : 3-dihydroxyacetophenone indicate a greater degree of chelation than the normal for a pyrocatechol derivative. 2 : 3-Dimethoxybenzaldehyde (I) and MgPhBr give 2 : 3-*dimethoxy-benzhydrol*, m.p. 79°, oxidised ($K_2Cr_2O_7$–$H_2SO_4$) to the -benzophenone (2 : 4-*dinitrophenylhydrazone*, m.p. 152°), which is demethylated to 2 : 3-*dihydroxybenzophenone*, m.p. 65°. (I) and Mg anisyl bromide form 2 : 3 : 4′-*trimethoxy-benzhydrol*, b.p. 250°/17 mm., which is oxidised to the -*benzophenone*, m.p. 86°, demethylated to 2 : 3 : 4′-*trihydroxybenzophenone*, m.p. 169°. The OH-ketones give strong yellow dyeings with $Al_2O_3$ mordant. F. R. S.

**Stereochemical investigations in the anisoin group.** A. McKenzie and D. J. C. Pirie (Ber., 1936, **69**, [*B*], 861—875).—*Me* r-p-*methoxymandelate*, m.p. 37—38°, obtained from MeI and *p*-OMe·$C_6H_4$·CH(OH)·$CO_2Ag$ [treatment of the acid with MeOH (EtOH) and $H_2SO_4$ gives impure products], is transformed by $NH_3$–EtOH at 0° into *p*-methoxymandelamide, m.p. 163—164°, which with Mg anisyl bromide affords *r*-anisoin (I), m.p. 112—113°. *r-p*-Methoxymandelic acid is resolved into its optical antipodes by cinchonine in $H_2O$. *d-p*-Methoxymandelic acid has m.p. 104—105°, $[\alpha]_{5461}^{20}$ +176·2° in $H_2O$, $[\alpha]_{5461}^{20\cdot3}$ +213·7° in $CHCl_3$ (other vals. recorded), whilst the l-*acid* has m.p. 104—105°, $[\alpha]_D$ −146·5° in $H_2O$. *Me* (+)-p-*methoxymandelate* has m.p. 63—64°, $[\alpha]_D^{20}$ +245°, $[\alpha]_{5461}^{20\cdot5}$ +295·8° in $CS_2$, $[\alpha]_D^{20}$ +119·7°, $[\alpha]_{5461}^{20}$ +144·1° in COMe, $[\alpha]_D^{20\cdot6}$ +140·3°, $[\alpha]_{5461}^{20\cdot6}$ +168·9° in EtOH, whereas m.p. 63—64°, $[\alpha]_D^{20}$ −245·8° in $CS_2$ are recorded for the corresponding (−)-*ester*. (+)-p-*Methoxymandelamide*, m.p. 143—144°, $[\alpha]_D^{21}$ +79·2°, $[\alpha]_{5461}^{21}$ +93·4° in $COMe_2$, $[\alpha]_D^{21}$ +90·6°, $[\alpha]_{5461}^{21}$ +107·6° in $H_2O$, is slowly racemised by EtOH–KOH, the steady fall in [α] being preceded by a slight rise. (−)-p-*Methoxymandelamide* has m.p. 143—144°, $[\alpha]_D^{20}$ −78·3° in $COMe_2$. (+)-*Anisoin* (II) has m.p. 132—133°, $[\alpha]_D^{20\cdot5}$ +60·9°, $[\alpha]_{5461}^{20\cdot5}$ +72·8° in $COMe_2$, $[\alpha]_D^{20\cdot5}$ +78°, $[\alpha]_{5461}^{20\cdot5}$ +93·3° in EtOH, $[\alpha]_D^{20\cdot3}$ +102·4°, $[\alpha]_{5461}^{20\cdot3}$ +122·4° in $CHCl_3$, $[\alpha]_D^{20\cdot5}$ +292°, $[\alpha]_{5461}^{20\cdot5}$ +357·2° in $CS_2$, whilst for (−)-*anisoin* (III), m.p. 132—133°, $[\alpha]_D^{19\cdot5}$ −60·2°, $[\alpha]_{5461}^{19\cdot5}$ −72·5° are recorded. (I) is transformed by warm 0·1*N*-KOH–EtOH into anisil (IV) and anisic acid. Under somewhat similar conditions (II) is slowly inactivated with production of (I) and (IV). (II) when heated at 140° for 10 min. in glass appears unchanged but gives (I) when heated for 2·5 hr. at 150°. (III) is fairly rapidly inactivated in piperidine or by a little $SOCl_2$ in $CHCl_3$. (—)-*Anisoin Me ether*, m.p. 60—61°, $[\alpha]_D^{20}$ −58·2°, $[\alpha]_{5461}^{20}$ −67·1° in $CHCl_3$, $[\alpha]_D^{20}$ −63·9°, $[\alpha]_{5461}^{20}$ −74·6° in EtOH, $[\alpha]_D^{18}$ +66° in heptane, is rapidly racemised by KOH–EtOH. r-*Anisoin acetate*, obtained by use of AcCl, has m.p. 94—95°. The corresponding (—)-*compound*, m.p. 77·5—78·5°, $[\alpha]_D^{16}$ −152°, $[\alpha]_{5461}^{16}$ −187° in $CHCl_3$, $[\alpha]_D^{16}$ −139°, $[\alpha]_{5461}^{16}$ −171° in EtOH, is rapidly hydrolysed by KOH–EtOH to (I). (II) is transformed by MgMeI into β-(—)-*methylhydroanisoin*, m.p. 102—103·5°, $[\alpha]_D^{20}$ −18·2°, $[\alpha]_{5461}^{20}$ −22·7° in $COMe_2$. r-β-*Methylhydroanisoin*, m.p. 82—83°, is amorphous. Catalytic reduction (Pt–$PtO_2$ in EtOH at 50—60°) of (III) leads to hydroanisoin, m.p. 172°, and, possibly, (+)-iso*hydroanisoin*. Reduction of non-cryst. *r*-anisoinoxime by Na–Hg in EtOH–AcOH affords *dianisylhydroxyethylamine* (IV), $OMe\cdot C_6H_4\cdot CH(OH)\cdot CH(NH_2)\cdot C_6H_4\cdot OMe$, m.p. 143—144° [*hydrochloride*, m.p. 212—213°; *platinichloride*, m.p. 177° (decomp.)], and the *iso*-base, m.p. 135—136°. Deamination of (IV) by $NaNO_2$ in dil. $H_2SO_4$ gives a substance, m.p. 100—101·5°, and *cis*-αβ-di-*p*-methoxyphenylethylene oxide, m.p. 142—143°.

H. W.

**Catalytic oxidations in aqueous solution. III. Oxidation of anthracene, quinol, and substituted quinols.** H. W. Underwood, jun., and W. L. Walsh (J. Amer. Chem. Soc., 1936, **58**, 646—647).—*p*-Benzoquinone and its Me, Cl-, and Br-derivatives are obtained in 90—94% yield by oxidation of the quinols with $NaClO_3$ and a little $V_2O_5$ in cooled 2% $H_2SO_4$; 1 : 4-$C_{10}H_6(OH)_2$ gives 93% of 1 : 4-naphthaquinone. Anthracene (in hot AcOH+2% $H_2SO_4$; caution necessary) similarly affords 90% of anthraquinone. Poor yields of oxidation products are obtained from $NH_2Ph$, *p*-$NH_2\cdot C_6H_4\cdot OH$, *p*-$C_6H_4(NH_2)_2$, and 1 : 4-$NH_2\cdot C_{10}H_6\cdot OH$. PhMe, phenanthrene, *cyclo*hexanol, borneol, and camphor were unaffected even on prolonged heating.

H. B.

**Synthesis of plumbagin.** L. F. Fieser and J. T. Dunn (J. Amer. Chem. Soc., 1936, **58**, 572—575).—The product from *m*-$C_6H_4Me\cdot COCl$ and Et sodio-α-acetylsuccinate in $Et_2O$ is hydrolysed (aq. KOH) to β-m-*toluoylpropionic acid*, m.p. 115—117° (purified through the *semicarbazone*, m.p. 191—193°), reduced (modified Clemmensen) to γ-m-*tolylbutyric acid*, m.p. 35—36°, the chloride of which is converted (method : Org. Synth., 1935, **15**, 77) into 1-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b.p. 129—132°/5 mm. This and Br in $CS_2$ at 5° give the 2-*Br*-derivative, m.p. 75—76°, converted by $NPhEt_2$ into 6-*methyl*-α-*naphthol*, m.p. 83—84°. Oxidation ($CrO_3$, AcOH at 0°—room temp.) of 6 : 1-$C_{10}H_6Me\cdot OAc$, b.p. about 124°/2 mm., affords 5-*acetoxy*-2-*methyl*-1 : 4-*naphthaquinone*, m.p. 117—118°, which with Zn dust and $Ac_2O$–NaOAc gives 1 : 4 : 5-*triacetoxy*-2-*methylnaphthalene*, m.p. 125—126°. Successive hydrolysis (5% NaOH and trace of $Na_2S_2O_4$ in $N_2$) and oxidation ($K_2Cr_2O_7$, dil. $H_2SO_4$) of this affords 5-*hydroxy*-2-*methyl*-1 : 4-*naphthaquinone* (I), m.p. 78—79°, which is identical with plumbagin [Ac derivative, m.p. 117—118° (lit. 115° and 138°)]. β-*p*-Toluoylpropionic acid, m.p. 124—126° [from $(\cdot CH_2\cdot CO)_2O$ and PhMe by the Friedel–Crafts reaction], is similarly converted into γ-*p*-tolylbutyric acid, m.p. 60—61°, and thence into 1-keto-7-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, an oil, 7-methyl-α-naphthol, m.p. 108—109° (acetate, m.p. 38—39°), and 8-hydroxy-2-methyl-1 : 4-naphthaquinone, m.p. 157—158° (*acetate*, m.p. 115—116°) [which, like (I), forms a coloured boroacetate conplex].

H. B.

**Anthracene. X. Preparation and hydrolysis of polyhydroxyanthraquinoneglucosides.** H. Foster [with J. H. Gardner] (J. Amer. Chem. Soc., 1936, **58**, 597—599).—1 : 5-Dihydroxyanthraquinone and acetobromo-*d*-glucose give (method : Takahashi, J. Pharm. Soc. Japan, 1925, **585**, 969) the *tetra-acetate*, m.p. 214·4°, of 1 : 5-*dihydroxyanthraquinone*-β-d-*glucoside* (I), m.p. 255·2°. Hydrolysis (method : A., 1935, 983) of (I) and 1 : 8-dihydroxy-, m.p. 240°, and 1 : 8-dihydroxy-3-methyl-, m.p. 255·2°, -anthraquinone-β-*d*-glucosides occurs in decreasing ease with 0·05*N*-KOH, dil. borax, and 0·05*N*-HCl, and gives the original dihydroxyanthraquinones; no reduction takes place. These results indicate that barbaloin is not an aloemodinarabinoside (Léger, A., 1917, i, 276). All m.p. are corr.

H. B.

**Synthesis of 1 : 2-phthaloylanthraquinone-6-carboxylic acid.** R. Scholl, G. von Hornuff, and H. K. Meyer (Ber., 1936, **69**, [*B*], 706—712).—1-Benzoylanthraquinone-2′ : 4′-dicarboxylic acid, m.p. 306—307° (decomp.), is obtained by chlorination of *m*-xylyl anthraquinonyl ketone (I) to $C_6H_4(CO)_2C_6H_3\cdot CO\cdot C_6H_3(CCl_3)_2$ in $C_6H_3Cl_3$ at 150° and treatment of the product with boiling 75% AcOH or by oxidising (I) with dil. $HNO_3$ at 180°; it is reduced by Zn dust and 30% NaOH at 170° to 1-*benzylanthracene*-2′ : 4′-*dicarboxylic acid* (II), m.p. 243—245° (decomp.), converted by boiling $POCl_3$ into *naphth*-2′ : 3′-1 : 2-*anthr*-10-*one*-6-*carboxylic acid* (III), which does not dissolve in $NH_3$–$H_2O$, but is slowly sol. in boiling KOH–$H_2O$ or KOH–EtOH with production of *naphth*-2′ : 3′-1 : 2-*anthran*-10-*ol*-6-*carboxylic acid* (III), more readily obtained from (II) and $ZnCl_2$ at 175°. Still more readily (II) is transformed by boiling $Ac_2O$ containing a trace of HI (*d* 1·7) into *acetic naphth*-2′ : 3′-1 : 2-*acetanthran*-10-*ol*-6-*carboxylic anhydride*, decomp. about 305° after softening at 190°, converted by boiling $C_5H_5N$–$H_2O$ into *naphth*-2′ : 3′-1 : 2-*acetanthran*-10-*ol*-6-*carboxylic acid*, decomp. 315°, which is hydrolysed by boiling NaOH to (IV). (III) is converted by red P and HI (*d* 1·7) at 190° into 9 : 10 : 1′ : 4′-*tetrahydronaphth*-2′ : 3′-1 : 2-*anthracene*-6-*carboxylic acid*, m.p. 290—300° after softening, which is oxidised by $CrO_3$ in AcOH to 1 : 2-*phthaloylanthraquinone*-6-*carboxylic acid*, incipient decomp. 340° (*$NH_4$ salt*; corresponding *diazine*, $C_{23}H_{10}O_4N_2$); attempts to decarboxylate it to *ang*.-phthaloylanthraquinone were unsuccessful. 4-Benzyl-1-methylnaphthalene-2′-carboxylic acid is converted by boiling $Ac_2O$ containing HI or HCl into 3-*methyl*-1 : 2-*benzanthran*-10-*yl acetate*, m.p. 195°.

H. W.

**Catalytic hydrogenation under high pressure. Essential oils and esters.** L. Palfray and S. Sabetay (Bull. Soc. chim., 1936, [v], 3, 682—687).—Catalytic hydrogenation (Ni) of certain essential oils under high pressure at about 240° causes partial reduction of esters to primary alcohols. Under similar conditions Et laurate affords dodecanol in 62% yield and some hydrocarbon, whilst $CH_2Ph{\cdot}CO_2Et$ gives β-*cyclo*hexylethyl alcohol, also obtained from $CH_2Ph{\cdot}CH_2{\cdot}OH$. H. W.

**Formation of nitrosites.** T. K. Gaponenkov (J. Gen. Chem. Russ., 1935, 5, 1485—1486).—Max. yields of nitrosite are obtained from β-phellandrene, $NaNO_2$, and AcOH when the solvent is 1 : 1 light petroleum–$Et_2O$, at low temp., and in absence of excess of AcOH. R. T.

**Polymerisation of pinene.** H. I. Waterman, J. J. Leendertse, and W. A. A. B. Koelensmid (Rec. trav. chim., 1936, 55, 7—12).—Polymerisation of pinene in $C_5H_{12}$ occurs at —15° with $AlCl_3$. No gases are evolved, and some light-coloured resin, almost free from O, is formed. The fractions of the product have been studied before and after hydrogenation. Vals. for $r_L$ after hydrogenation suggest that polymerisation takes place without the opening or closing of rings. Pinene when hydrogenated (Ni–kieselguhr) at 200—250° (pressure about 100 kg. per sq. cm.) gives a product agreeing fairly well in properties with pinane in the lit. H. G. M.

***endo–exo*-Isomerism in alicyclic alcohols of borneol type. I.** G. Komppa and S. Beckmann (Annalen, 1936, 522, 137—150; cf. Biltz, A., 1899, i, 297, ii, 634; Hückel *et al.*, A., 1935, 745).—The mol. wts. of the 14 *sec.*-alcohols containing the 1 : 2 : 2-di*cyclo*heptane ring are determined (f.-p. method in $C_6H_6$) for different concns. and the % association ($A$) calc. for a concn. of 0·06 mol. per 100 g. $C_6H_6$. The alcohols form 3 groups : (i) $A = 54$—58, those with no substituent near the OH; (ii) $A = 33$—44, those with the OH "screened" by 1 substituent; (iii) $A = 19$—24, those with the OH "hindered" by substituents from 2 sides. The effect of, *e.g.*, $C_7{\cdot}Me$ is of decisive importance; $C_6$ has little or no effect. Borneol, 4-methylborneol, and α-fenchocamphorol (*apo*borneol) are considered to have *endo*-OH, whilst *iso*borneol, 4-methyl*iso*borneol, and *iso*fenchol have *exo*-OH. α-Santenone alcohol and α-santenol have *endo*- and *exo*-OH, respectively; both contain $C_7{\cdot}Me$ in the *trans* position. Definite conclusions are not yet possible for α- and β-norborneols, camphenilols I and II, β-fenchocamphorol, and α-fenchol. H. B.

**Racemisation and camphene transformation.** J. Houben and E. Pfankuch (Ber., 1936, 63, [*B*], 899—901).—A reply to Nametkin *et al.* (A., 1935, 89). H. W.

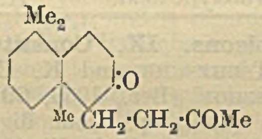
**Hydrogenation of carbonyl compounds.**—See this vol., 686.

**Preparation of *d*-*trans*-π-oxocamphor from *iso*ketopinic acid.**—See B., 1936, 444.

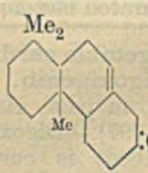
**4-Methyl*iso*santenol and 4-methylsantenylamine.** G. Komppa and G. A. Nyman (Ber., 1936, 69, [*B*], 712—716; cf. A., 1935, 865).—4-Methylsantenol, m.p. 33—34·5° (*loc. cit.*), is transformed by *o*-$C_6H_4(CO)_2O$ in $C_5H_5N$ at 100° into 4-*methylsantenyl H phthalate*, m.p. 135—136°, hydrolysed to the alcohol, m.p. 36—37°. Reduction of 4-methylsantenone with Na and EtOH affords 4-*methyliso-santenol*, b.p. 200—200·5°, m.p. 40—42° (*H phthalate*, m.p. 143—144°; *phenylurethane*, m.p. 93—94·5°). 4-*Methylsantenoneoxime*, m.p. 110·5—111·5° (*Bz* derivative, m.p. 83—84°), is reduced by Na and boiling abs. EtOH to 4-*methylsantenylamine*, b.p. 62°/8 mm. [*hydrochloride* (I); *aurichloride*, m.p. about 163° after softening; *platinichloride*, m.p. 266—269°; *picrate*, m.p. 242—244° (decomp.); *Bz* derivative, m.p. 153·5—154·5°]. Treatment of (I) with $HNO_2$ does not give a homogeneous alcohol. H. W.

**Diterpene alcohol from the wood of *Dacrydium biforme*. II. Ozonisation of manool.** J. R. Hosking (Ber., 1936, 69, [*B*], 780—785; cf. A., 1935, 1127).—Ozonisation of manool (I) in $CCl_4$ at 0° and decomp. of the ozonide by $H_2O$ at 100° gives the non-cryst. *diketone* (II), b.p. 159—160°/0·1 mm. (non-cryst. compounds with $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ and $NH_2OH$ and ill-defined derivatives with aminoguanidine or picric acid), which does not reduce dil. $KMnO_4$ at 20°. If (II) is warmed with NaOEt or heated with HCl at 0° followed by NaOH–EtOH it is transformed into the cryst. *ketone* (III), m.p. 71° (*semicarbazone*, m.p. 188°). Treatment of (II) with 2% NaOH–EtOH at 20° or with piperidine in $C_6H_6$ affords the *compound* (IV), m.p. 199°, which is saturated and contains 1 active OH (Zerevitinov). Excess of MgMeI converts (IV) with loss of $2H_2O$ into the liquid hydrocarbon (V), b.p. 127—130°/0·1 mm. (hydrogenated to the substance $C_{18}H_{32}$, b.p. 120°/0·1 mm.), which is dehydrogenated by Se at 340° to 1 : 7-dimethylphenanthrene. Oxidation of (I) by $KMnO_4$ (=8O) in $COMe_2$ gives an unsaturated *ketone*, $C_{17}H_{28}O$, b.p. 137—138°/0·1 mm. (*semicarbazone*, m.p. 185—186°), hydrogenated ($PtO_2$ in EtOAc) to a saturated ketone (*semicarbazone*, m.p. 199—200°). H. W.

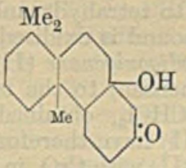
(II.)



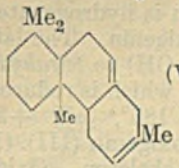
(III.)



(IV.)



(V.)

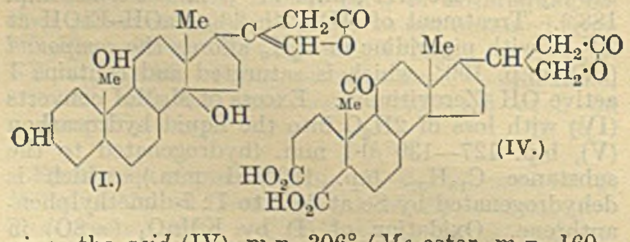


**Biochemistry of micro-organisms. XLIX. Palitantin, a metabolic product of *Penicillium palitans*, Westling.** J. H. Birkinshaw and H. Raistrick (Biochem. J., 1936, 30, 801—808).—Three strains of the mould, grown in Raulin–Thom glucose medium, yielded *palitantin* (I), $C_{14}H_{22}O_4$, m.p. 163—165° [*semicarbazone*, m.p. 212—213° (decomp.); *phenylhydrazone*, m.p. 175—176°; *oxime*, m.p. 104—106°; 2 : 4-*dinitrophenylhydrazone*, m.p. 209°; *di-p-bromobenzoate*, m.p. 153—154°]. (I), which contains ·CHO, 2 OH, and ≮ two double linkings, is hydrogenated (Pd–C) to *tetrahydropalitantin* (II), m.p. 116°

(*semicarbazone*, m.p. 188—189°), further reduced (Na–Hg) to α-, m.p. 142—143°, and β-*hexahydropalitantin*, m.p. 98—99°, and oxidised (NaOI) to *tetrahydropalitantic acid*, m.p. 110° (to an opaque liquid clearing at 135°). Oxidation of (I) by $HgI_2$–KI affords *palitantic acid*, $C_{14}H_{22}O_5$, m.p. 145—148°, whilst that by $Ag_2O$ followed by esterification with $CH_2N_2$ and treatment with aq. $N_2H_4,H_2O$ yields the *dihydrazide*, m.p. 201—202°, of a dicarboxylic acid, $C_{13}H_{20}O_5$ (or of its lactone); similar treatment of (II) gives the *dihydrazide*, m.p. 188—190°, of a dicarboxylic acid, $C_{13}H_{24}O_5$ (or of its lactone).
F. O. H.

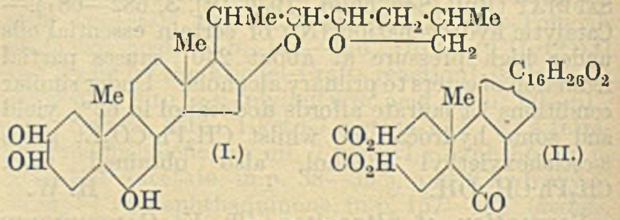
**Bitter principles of Colombo root. IV.** K. Feist and R. Brachvogel (Annalen, 1936, 522, 185—190).—KOH-fusion of columbin (I) gives some 2-methylterephthalic acid in addition to 2 : 4-$C_6H_3Me_2$·$CO_2H$ (A., 1935, 1245). (I) is reduced by Pd-black and boiling tetrahydronaphthalene to hydrochasmanthic acid (*ibid.*, 864), and thus contains a lactone ring. Chasmanthin is not oxidised by $SeO_2$, but its Me ether with 5% $KMnO_4$ in a slightly alkaline medium affords *merochasmanthic acid Me ether*, $C_{16}H_{20}O_8$, m.p. 248° (decomp.) (*Me*$_2$ ester, m.p. 254—255°, hydrolysed with difficulty), which appears to be a saturated lactonic dicarboxylic acid. H. B.

**Vegetable cardiac poisons. IX. Constitution of digoxigenin.** R. Tschesche and K. Bohle [with, in part, H. Grasshof] (Ber., 1936, 69, [*B*], 793—797).—Digoxigenin (I) (prep. from digilanid described) is converted into anhydrodigoxigenin, which is hydrogenated ($PtO_2$) to tetrahydroanhydrodigoxigenin. The latter compound is oxidised ($CrO_3$ in AcOH) to *tetrahydroanhydrodigoxigenone* (II), m.p. 290°, which is reduced (Clemmensen) to the lactone, m.p. 185°, $[\alpha]_D^{21}$ +34·5° in $CHCl_3$, obtained from digitoxigenin (III). (I) and (III) have therefore the same skeleton. Oxidation of (II) with $CrO_3$ in AcOH gives the *acid* (IV), m.p. 306° (*Me* ester, m.p. 160—161°), which passes when heated into the *ketone*, $C_{22}H_{30}O_4$, m.p. 228—229°, and is hydrogenated to the *substance*, $C_{23}H_{34}O_7$, m.p. 266—267°. (I) has probably the structure shown. H. W.

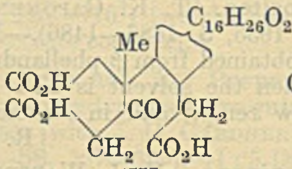


(I.) (IV.)

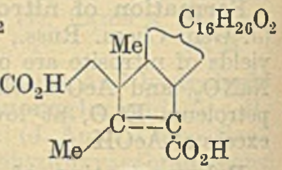
**Saponins of the *cyclo*pentanohydrophenanthrene group. IV. Constitution of gitogenin and digitogenin.** R. Tschesche and A. Hagedorn (Ber., 1936, 69, [*B*], 797—805).—Mainly theoretical. Reasons are advanced for assigning the structure (I) to digitogenin. Digitogenic acid, obtained by cautious oxidation of (I) with $CrO_3$, is shown to be a γ-CO-acid (II), which accounts for its inability to lose $CO_2$ (cf. Windaus *et al.*, A., 1925, i, 1082). Oxydigitogenic acid, obtained from (II) and $KMnO_4$, its decarboxylation product, and the enol-lactone obtained by heating its esters are formulated according to (III), (IV), and (V).



(I.) (II.)

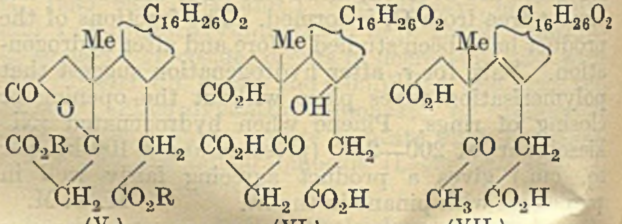


(III.)

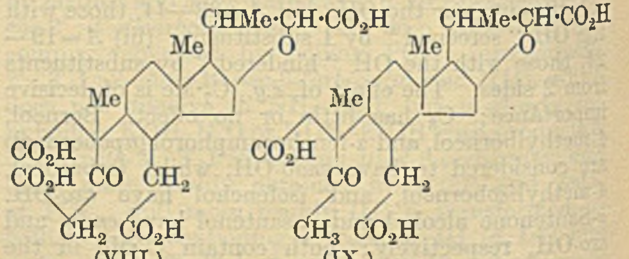


(IV.)

Digitic acid (VI) obtained by drastic oxidation of (III) contains a new *tert.*-OH (Zerevitinov) probably at 8-C or 9-C. The constitutions (VI) and (VII) are assigned to it and anhydrodigitic acid obtained from it by loss of $CO_2$ and $H_2O$ when treated with AcOH and HCl. The pentacarboxylic acid, $C_{26}H_{38}O_{12}$, of Windaus *et al.* (*loc. cit.*) is shown to be a tetracarboxylic acid (VIII)+$1H_2O$ very firmly attached. It loses $CO_2$ when heated and gives the tricarboxylic acid (IX)+$1H_2O$, the composition of which is confirmed by analyses of the anhydrous Me ester.

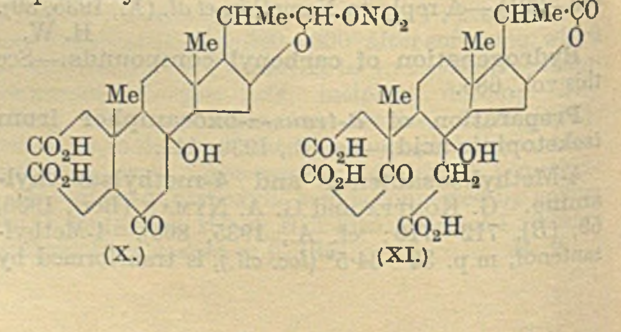


(V.) (VI.) (VII.)



(VIII.) (IX.)

The lactol nitrate obtained by oxidation of digitoic acid with $HNO_3$ (Windaus and Shah, A., 1926, 404) and the ketocarboxylic acid obtained by treating it with $KMnO_4$ are formulated according to (X) and (XI), respectively.

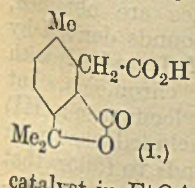


(X.) (XI.)

The production of $CO_2H·CHMe·CH_2·CO_2H$ from gitogenin and (I) is readily understood but $CO_2H·CHMe·[CH_2]_2·CO_2H$ appears to be derived by complete rupture of the whole ring system. H. W.

**Phenol- and methylglycol- [β-methoxyethyl alcohol-]lignin from spruce wood.** W. Fuchs (J. Amer. Chem. Soc. 1936, **58**, 673—680).—PhOH-lignin (I) [large-scale prep. from spruce wood flour (*A*), PhOH, and conc. HCl at 85—90°] is partly adsorbed by activated C from an EtOH-solution. The unadsorbed material is then fractionated by $Et_2O$, EtOAc, and aq. $Na_2CO_3$; successive extraction of the C with EtOH gives further fractions. Similarly, methylglycol-lignin (II) [prep. from (*A*), $OMe·CH_2·CH_2·OH$, and conc. HCl at 121° under pressure] is partly adsorbed by C from a $COMe_2$ solution; fractionation of the unadsorbed part is effected with $Et_2O$, $CHCl_3$, and aq. $Na_2CO_3$. Several of the fractions are analysed for C, H, and OMe (using AcOH–HI; elimination of $OMe·CH_2·CH_2·OH$ does not occur to any appreciable extent); acetylation ($Ac_2O$+0·2% conc. $H_2SO_4$ at 100°) gives products which are insol. in dil. alkali (showing absence of $CO_2H$) but sol. in $C_6H_6$ (cf. Wedekind and Katz, A., 1929, 799). Potentiometric titration indicates, however, that the fractions are mixtures of several compounds. Contrary to Hägglund, the combined PhOH (2·4—26·5%) in fractions of (I) is eliminated by treatment with red P and AcOH–HI (or AcOH–HBr, whereby a sugar-like substance is also produced), thus proving the presence of $>C(OPh)_2$ (cf. A., 1929, 1282) or ⁝C·OPh (cf. Brauns and Hibbert, A., 1935, 1373). KOH-fusion of fractions from (I) and (II) gives *p*-$OH·C_6H_4·CO_2H$ (0·8—11% of lignin), 3 : 4-$(OH)_2C_6H_3·CO_2H$ (4·3—16·1% of lignin), *o*-$C_6H_4(OH)_2$, and (probably) phenol-2 : 4-dicarboxylic acid; oxidation (AcOH–$HNO_3$) affords picric and benzenecarboxylic acids. A possible structure for spruce lignin is given. The original must be consulted for details. H. B.

**Picrotoxin. II. Picrotone and picrotonol.** D. Mercer and A. Robertson (J.C.S., 1936, 288—294).—Oxidation ($KMnO_4$) of picrotonol yields αα-4-trimethylphthalide-3-acetic acid (I), decarboxylated to tetramethylphthalide, in agreement with Horrmann and Hagendorn (A., 1921, i, 347) and contrary to Angelico (A., 1910, i, 404). β-*o*-Tolylpropionyl chloride, obtained from *o*-toluoyl chloride and Et sodiomalonate, with $AlCl_3$–$C_6H_6$ followed by amyl nitrite-HCl, gives 2-*oximino*-4-*methyl*-1-*hydrindone*, m.p. 215° (decomp.). The oximino-compound with *p*-toluenesulphonyl chloride yields o-*tolylacetonitrile-3-carboxylic acid*, m.p. 142—143°, hydrolysed to 6-*methylbromophthalic acid*, m.p. 195—196° (*anhydride*, m.p. 150°), also obtained with $COMe_2$ from (I) and KOH. Hydrolysis of picrotoxinin ozonide gives $CH_2O$, $HCO_2H$, and picrotoxinone, indicating the presence of ⁝C⁝$CH_2$ in picrotoxinin (II). Hydrogenation (Pt) of (II) affords α-dihydropicrotoxinin, m.p. 252°, which with $H_2SO_4$ forms dihydropicrotoxic acid (III), whilst with a Pd catalyst in EtOAc, β-*dihydropicrotoxinin*, m.p. 256—257°, $[\alpha]_D^{20}$ −24·69° in $COMe_2$, is obtained, unaffected by $H_2SO_4$. Hydrogenation with Pd in EtOH–HCl gives a substance, which is a mixture of at least three compounds, and with $H_2SO_4$ yields (III) and picrotonol (p-*nitrobenzoate*, m.p. 155°). (III) and MeI–$Ag_2O$ form *Me* O-*dimethyldihydropicrotoxate*, m.p. 146—147°, $[\alpha]_D^{20}$ +95·93° in $CHCl_3$, hydrolysed to the *acid*, m.p. 206—207°. The possible structure of picrotoxinin is discussed on the basis of the C-skeleton for picrotonol. F. R. S.



(I.)

**Gentiopicrin. I.** Y. Asahina, J. Asano, Y. Tanase, and Y. Ueno (Ber., 1936, **69**, [*B*], 771—779).—Gentiopicrin (I), obtained from the root of *Gentiana scabra*, Bunge, var. *Buergeri*, Maxim, has m.p. (anhyd.) 191°, m.p. (+0·5$H_2O$) 121°. It gives a dark red condensation product with $NHPh·NH_2$, a p-*nitrophenylhydrazide*, $C_{22}H_{27}O_{11}N_2$, m.p. 199° (decomp.), and an iso*propylidene* derivative, m.p. 228°. When hydrolysed by emulsin at room temp. it affords insol. gentiogenin (II) (cf. Tanret, A., 1905, i, 655) and sol. *eugentiogenin* (III), $C_{10}H_{10}O_4$, m.p. 123°, [α] ±0° in $CHCl_3$ (p-*nitrophenylhydrazone*, decomp. 180°), which does not give Tanret's reaction or a blue colour after dissolution in alkali and acidification with conc. $H_2SO_4$. (II), m.p. 184° (decomp.), is $(C_{10}H_{10}O_4)_2$ and is regarded as a dimeric product from (III). Hydrolysis of (I) with KOH–EtOH establishes the presence of 1 Ac. Oxidation of (I) with $KMnO_4$ after hydrolysis yields AcOH, whereas $H_2O_2$ affords $(·CH_2·CO_2H)_2$. (I) and $Ac_2O$ in $C_5H_5N$ at 100° give *gentiopicrin tetra-acetate* (IV), m.p. 139°, $[\alpha]_D^{17}$ −164·7° in $CHCl_3$, which yields $CH_2O$ after ozonolysis. Hydrogenation (Pd–C in EtOAc) of (I) leads to *tetrahydrogentiopicrin* (V), m.p. 190°, $[\alpha]_D^{20}$ − 75·13° in abs. EtOH, which does not yield a volatile acid when boiled with excess of $Ba(OH)_2$–$H_2O$, and is converted by $Ac_2O$ in $C_5H_5N$ into *tetrahydrogentiopicrin tetra-acetate*, m.p. 208°, also obtained by hydrogenation of (IV). Oxidation of (V) with $KMnO_4$ affords $EtCO_2H$, whilst dry distillation of it gives $Pr^{\alpha}CHO$. (V) is hydrolysed by emulsin to *tetrahydroprotogentiogenin* (VI) $C_{10}H_{14}O_4$, m.p. 98°, $[\alpha]_D^{20}$ + 214·9° [p-*nitrophenylhydrazone*, m.p. 184° (decomp.)], which immediately reduces $MnO_4'$ but does not give a colour with $FeCl_3$. Hydrogenation (Pd–C in $H_2O$) of (I) affords *hexahydroprotogentiogenin* (VII), $C_{10}H_{16}O_4$, m.p. 140°, $[\alpha]_D^{15}$ +161·0° in abs. EtOH, which does not reduce $NH_3$–$Ag_2O$ or $KMnO_4$ in $COMe_2$ [also obtained from (VI)], hexahydrogentiopicrin and glucose. Oxidation of (VII) by $CrO_3$ in AcOH gives a *compound*, $C_{10}H_{14}O_4$, m.p. 93°, $[\alpha]_D^{20}$ −30·53° in abs. EtOH. H. W.

**Saponins. XI. Sapogenin of the roots of *Momordica cochinchinensis* (Laur), Spreng.** S. Kuwada and Y. Fuwa (J. Pharm. Soc. Japan, 1935, **55**, 467—473).—Momordin (saponin from *M. cochinchinensis*) is hydrolysed to *momorgenin* (I), $C_{30}H_{48}O_3$, decomp. 309·8° (corr.), $[\alpha]_D$ +78·3° in $COMe_2$ [*K* salt; *monoacetate*, m.p. 266° (corr.); *Me* ester (II), m.p. 203° (*Ac* derivative, m.p. 220°); *benzoate*, m.p. 261° (*Me* ester, m.p. 269°)]. (II) does not depress the m.p. of Me oleanolate and (I) resembles oleanolic acid in many respects. Ch. Abs. (*r*)

**Saponin of the seeds of *Esculus turbinata*, Blume. I.** T. Matsukawa (J. Pharm. Soc. Japan, 1935, 55, 350—357).—*Japoescinin*, $C_{65}H_{101}O_{30}$, m.p. about 200° (decomp.), is obtained from Japanese *E. turbinata* by an improved method; it is hydrolysed to a *prosapogenin*, $C_{59}H_{94}O_{25}$, m.p. 210° (corr.) (*dibromide*, m.p. 175°), further hydrolysed to *japoescigenin* (I), $C_{35 \text{ or } 36}H_{58 \text{ or } 60}O_7$, m.p. 258° (corr.), possibly isomeric with Winterstein's escigenin (A., 1931, 1159). (I) contains 4 active H (Zerevitinov) and on hydrolysis yields *japoescigenol* (II), $C_{30 \text{ or } 31}H_{52 \text{ or } 51}O_6$, m.p. 307° [*monobromide*, m.p. 196° (decomp.); *tetra-acetate*, m.p. 198° (corr.)], and tiglic acid. (II) contains 5 active H (probably 5 OH, the remaining O being in a bridge) and one double linking. Ch. Abs. (*r*)

**Hydrogenation of acetylene derivatives. XXII. Dihydroxy*cyclo*hexylacetylene.** J. S. Salkind [with T. E. Zalesskaja, D. I. Rozanov, and G. V. Tschelincev] (J. Gen. Chem. Russ., 1935, 5, 1723—1727).—1 : 1'-Dihydroxy-1 : 1'-di*cyclo*hexylacetylene (I) ($Ac_2$ derivative, b.p. 164—170°, m.p. 45·5—46·5°) and Br in $CHCl_3$ afford *αβ-dibromo-αβ-di*cyclo*hexylethylene* 1 : 1'-*oxide*, m.p. 106·5—107·5°. (I) is readily hydrogenated (Pd) to 1 : 1'-*dihydroxy*-1 : 1'-*di*cyclo*hexylethylene*, m.p. 152°, which yields adipic acid when oxidised with $KMnO_4$. R. T.

**Conversion of furfuraldehyde into hydrocarbons.** N. A. Orlov and O. A. Rjabtschenko (J. Appl. Chem. Russ., 1936, 9, 249—253).—Furfuraldehyde reacts with $H_2$ in presence of $MoS_3$ (270°/150 atm.; 3—4 hr.) to yield sylvan, tetrahydrosylvan, EtOH, and CHMePr·OH; at 330—350° (1·5—2 hr.) the product consists chiefly of *n*-pentane, together with unsaturated condensation products. R. T.

**True effect of cyclisation on the "colour" of molecules. Ultra-violet absorption of *o*-methoxyacetophenone, β-coumaranone, and γ-chromanone.** (Mme.) Ramart-Lucas and M. van Cowenbergh (Bull. Soc. chim., 1935, [v], 2, 1381—1383).—The ultra-violet absorption spectra of *o*-OMe·$C_6H_4$·COMe, γ-chromanone, and β-coumaranone in EtOH are closely similar, displacement towards the visible increasing in the order given, *i.e.*, being the greater the smaller is the no. of atoms in closed chain. J. W. B.

**Synthesis of 1 : 2-diphenylcoumarones.** B. I. Arventi (Bull. Soc. chim., 1936, [v], 3, 598—603).—When heated at 250—290° *o*-benzoyloxydiphenylacetic acids lose $CO_2$ and $H_2O$ with production of 1 : 2-diphenylcoumarones. Thus, *o*-benzoyloxydiphenylacetic acid at 290° gives $CO_2$, $H_2O$, BzOH, 1 : 2-*diphenylcoumarone*, m.p. 123° (identified by oxidation with $CrO_3$ to *o*-$C_6H_4$Bz·OH), and *o*-hydroxydiphenylacetolactone. *p*-$C_6H_4$Cl·OH and OH·CHPh·$CO_2H$ yield 4-chloro-2-hydroxydiphenylacetic acid, the Bz derivative of which at 260—280° gives 4-*chloro*-1 : 2-*diphenylcoumarone*, m.p. 118°, oxidised to 5-*chloro*-2-*benzoyloxybenzophenone*, m.p. 112°, whence 5-chloro-2-hydroxybenzophenone, m.p. 94—95°. 1 : 2-*Diphenyl*-4-*methylcoumarone*, m.p. 114°, and 1 : 2-*diphenyl*-5-*methylcoumarone*, m.p. 93°, are described. H. W.

**Reaction between quinones and sodium enolates. IV. ψ-Cumoquinone and sodio-acetoacetic and -malonic esters.** L. I. Smith and C. W. MacMullen (J. Amer. Chem. Soc., 1936, 58, 629—635).—Trimethyl-*p*-benzoquinone (ψ-cumoquinone) (I) and CHNaAc·$CO_2$Et in EtOH give 4-*hydroxy*-1 : 3 : 5 : 6-*tetramethylcoumarone* (II), m.p. 138—139° (*benzoate*, m.p. 145—145·5°; *Me ether*, m.p. 60—61°), some 4-*hydroxy*-3 : 5 : 6-*trimethyl*iso*coumaranone* (III), m.p. 197—198°, and a resin [which when treated with Zn dust and aq. AcOH affords a considerable amount of (III)]. When the reaction is carried out in $C_6H_6$, (II) is the main product. (II) and (III) arise by ring-closure (in two ways) of the intermediate 2 : 5 : 3 : 4 : 6-$(OH)_2C_6Me_3$·CHAc·$CO_2$Et and subsequent ketone or acid fission; a coumarin is not produced (cf. this vol., 480). (III) is the sole product from (I) and $CHNa(CO_2Et)_2$. Methylation ($Me_2SO_4$, MeOH–KOH) of (III) gives 3 : 6-*dimethoxy*-2 : 4 : 5-*trimethylphenylacetic acid* (IV), m.p. 158—159°. 2 : 4 : 5-$C_6H_2Me_3$·CHO (V) [from ψ-cumene (VI), $Zn(CN)_2$, and HCl in $C_6H_6$] is reduced (Zn, aq. AcOH) to the impure *acetate*, b.p. 141—150°/9 mm., of 2 : 4 : 5-*trimethylbenzyl alcohol*, m.p. 83—83·5° (cf. Krömer, A., 1891, 1351); the *chloride*, b.p. 110°/5 mm. [prepared using conc. HCl or by chloromethylation (method: von Braun and Nelles, A., 1934, 879) of (VI)], with aq. EtOH–NaCN gives the *nitrile*, b. p. 133—137°/4 mm., m.p. 9—10°, of 2 : 4 : 5-trimethylphenylacetic acid (VII), m.p. 128—129° (lit. 118°). (VII) is also obtained by reduction (red P, 45% HI, AcOH) of 2 : 4 : 5-*trimethylmandelic acid*, m.p. 133—135° [from (V); method: Corson *et al.*, Org. Synth., 1932, 1, 329], and from 2 : 4 : 5-$C_6H_2Me_3$·COMe by Willgerodt and Scholtz' method (A., 1910, i, 392). 3 : 6-*Dinitro*-2 : 4 : 5-*trimethylphenylacetic acid*, m.p. 203—203·5°, from (VII) and fuming $HNO_3$ in $CHCl_3$ + conc. $H_2SO_4$ at 0°—room temp., is reduced by $H_2$ (40 lb.), $PtO_2$, EtOH to 5-*nitro*-, and by $H_2$ (1300 lb.), Raney Ni, EtOH at 80° to 5-*amino*-, m.p. 260—261°, -4 : 6 : 7-*trimethyloxindole*. The latter is hydrolysed by aq. $Ba(OH)_2$ at 160° to 3 : 6-diamino-2 : 4 : 5-trimethylphenylacetic acid; diazotisation of this and heating the resulting solution gives a product, m.p. 176—183°, which with Zn and AcOH affords (III). HCl passed into 3 : 6-dimethoxy-ψ-cumene, aq. $CH_2O$, and conc. HCl at 70° gives 3 : 6-*dimethoxy*-2 : 4 : 5-*trimethylbenzyl chloride*, b.p. 134—135°/3·5 mm., m.p. 63—63·5°, converted by aq. EtOH–NaCN into the *nitrile*, m.p. 90—91°, of (IV). H. B.

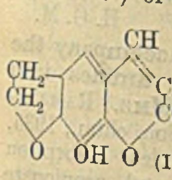
**Hydroxy-carbonyl compounds. XI. Phosphoryl chloride as a condensing agent.** (Miss) I. Goodall and A. Robertson (J.C.S., 1936, 426—428).—*p*-Xylenol does not condense with $CH_2Ac·CO_2Et$ in presence of $POCl_3$ but with Et α-methyl- (I), Et α-ethyl- (II), and Et α-benzyl-acetoacetate (III), and Et benzoylacetate (IV), chromones are obtained, identical with the respective compounds derived by the $P_2O_5$ method. Condensation of (I) and (II) with *m*-4-xylenol ($POCl_3$) also yields chromones, but $CH_2Ac·CO_2Et$ gives 4 : 6 : 8-trimethylcoumarin: (III) and (IV) do not react. It is concluded that with $POCl_3$ the course of the reaction tends to follow that obtaining with $P_2O_5$. The following have been prepared : 2 : 5 : 8-*trimethyl*-, m.p. 81°, 2 : 3 : 5 : 8-*tetramethyl*-, m.p. 96·5—97·5°, 2 : 5 : 8-*trimethyl*-3-*ethyl*-, m.p. 86·5°, 3-*benzyl*-2 : 5 : 8-*trimethyl-chromone*, m.p. 101°, and 2-(3′ : 4′-*methylenedioxystyryl*)-5 : 8-*dimethyl*-, m.p. 183°, -3 : 5 : 8-*trimethyl*-, m.p. 226°, -5 : 8-*dimethyl*-3-*ethyl*-, m.p. 153°, and -3-*benzyl*-5 : 8-*dimethyl-chromone*, m.p. 222°, and 5 : 8-*dimethylflavone*, m.p. 171°. F. R. S.

**Synthesis of a natural colouring matter.** R. Robinson (Proc. Roy. Inst., 1936, 29, 41—56).—An account of the synthesis of pelargonin chloride.

**Amino-alcohols derived from 1 : 2 : 3 : 4-tetrahydrodibenzfuran.** R. A. Robinson and E. Mosettig (J. Amer. Chem. Soc., 1936, 58, 688—689; cf. this vol., 209).—7-*Bromoacetyl*-1 : 2 : 3 : 4-*tetrahydrodibenzfuran*, m.p. 81—82° (all m.p. are corr.), and the appropriate base give 7-dimethylamino- (*hydrochloride*, m.p. 244—247°), 7-diethylamino- (*hydrochloride*, m.p. 202—210°), 7-piperidino- (*hydrochloride*, m.p. 235—239°), and 7-1′ : 2′ : 3′ : 4′-tetrahydro*iso*quinolino- (*hydrochloride*, m.p. 260—264°), -acetyl-1 : 2 : 3 : 4-tetrahydrodibenzfurans. 7-β-Dimethylamino- (*hydrochloride*, m.p. 220—222°), 7-β-piperidino- (*hydrochloride*, m.p. 230—232°), and 7-β-1′ : 2′ : 3′ : 4′-tetrahydro*iso*quinolino- (*hydrochloride*, m.p. 197—200°), -α-hydroxyethyl-1 : 2 : 3 : 4-tetrahydrodibenzfurans are prepared (with difficulty) by catalytic reduction of the $NR_2{\cdot}CH_2{\cdot}CO$ derivatives. H. B.

**Constitution of oroxylin.** R. C. Shah, C. R. Mehta, and T. S. Wheeler (Current Sci., 1935, 4, 406).—Oroxylin, m.p. 231—232° (lit. 225°), from the root bark of *Oroxylum indicum*, Vent., has 1 OMe (cf. J.C.S., 1901, 79, 954) and is shown by demethylation and by methylation to be 5 : 7-dihydroxy-6-methoxyflavone. The colour reaction obtained by previous workers from (I) with dil. alkali is due to baicalein (5 : 6 : 7-trihydroxyflavone) present as an impurity. H. G. M.

**Natural coumarins. XVII. Synthesis of xanthotoxin.** E. Späth and M. Pailer (Ber., 1936, 69, [*B*], 767—770).—Hydrogenation (Pd–C in AcOH at 40—45°) of 6 : 7-dihydroxycoumaranone affords 6 : 7-*dihydroxycoumaran* (I), m.p. 112°, and a substance, m.p. 132°. (I), lactic acid, and conc. $H_2SO_4$ at 120° afford 4′ : 5′-*dihydroxanthotoxol* (II), m.p. 202°, converted by $CH_2N_2$ in MeOH into 4′ : 5′-*dihydroxanthotoxin*, m.p. 163°, which is dehydrogenated (Pd-sponge at 170°) to xanthotoxin, m.p. 146°. H. W.



(II.)

**Analogues of rotenone and related compounds. I. Chromeno-(3′:4′:4:3)-coumarins.** W. Hilton, R. W. H. O'Donnell, F. P. Reed, A. Robertson, and G. L. Rusby (J.C.S., 1936, 423—426).—Resorcinol and Et 3-hydroxy-6 : 7-dimethoxy-Δ³-chromene-4-carboxylate (I) with $H_2SO_4$ give 7-*hydroxy*-6′ : 7′-*dimethoxychromeno*-(3′ : 4′ : 4 : 3)-*coumarin* (+$H_2O$), m.p. 245° (*acetate*, m.p. 220—221°). Similar condensation of (I) with the appropriate phenol and either $H_2SO_4$ or HCl–EtOH leads to the following -*chromeno*-(3′ : 4′ : 4 : 3)-*coumarins* : 7 : 8-*dihydroxy*- (+$H_2O$), m.p. 274° (decomp.) (*diacetate*, m.p. 232—233°), and 5 : 7-*diacetoxy*-6′ : 7′-*dimethoxy*-, m.p. > 300° ; 7-*hydroxy*-6′ : 7′-*dimethoxy*-, m.p. 230—231° (*acetate*, m.p. 137°), 7-*hydroxy*-7′-*methoxy*-, m.p. 228° (*acetate*, m.p. 219°), and 7-*hydroxy*-8′-*methoxy*-8-iso-*amyl*-, m.p. 245° (*acetate*, m.p. 188°) ; 7-*hydroxy*-, m.p. 266° (*acetate*, m.p. 222°), 7 : 8-*dihydroxy*-, m.p. 254° (*diacetate*, m.p. 231·5°), and 5 : 7-*dihydroxy*-7′-*methoxy*-, m.p. 309° (*diacetate*, m.p. 253°) ; 7-*hydroxy*-, m.p. 269° (*acetate*, m.p. 232°), 7 : 8-*dihydroxy*-, m.p. 277° [*diacetate*, m.p. 264° (decomp.)], and 5 : 7-dihydroxy-8′-methoxy- (*diacetate*, m.p. 224°). *Et phenoxyacetic-2-acetate*, m.p. 48—49°, and Na in PhMe afford Et chroman-3-one-4-carboxylate, which with resorcinol in HCl–EtOH yields 7-*hydroxychromeno*-(3′ : 4′ : 4 : 3)-*coumarin*, m.p. 276—278° (*acetate*, m.p. 214—215°). F. R. S.

**Synthesis of rotenone and its derivatives. IX.** R. W. H. O'Donnell, F. P. Reed, and A. Robertson (J.C.S., 1936, 419—422).—The Et ester of 6-*methoxyphenoxyacetic-2-acetic acid*, m.p. 166°, prepared from the azlactone of Et 2-aldehydo-6-methoxyphenoxyacetate, NaOH, and $H_2O_2$, is cyclised (Na) to *Et* 3-*hydroxy*-8-*methoxy*-Δ³-*chromene*-4-*carboxylate* (I), m.p. 87°, the *Ac* derivative, m.p. 72°, of which is reduced ($H_2$–Pt) and hydrolysed to 8-*methoxychroman*-4-*carboxylic acid*, m.p. 110°. (I) is reduced ($H_2$–Pt) to *Et* 3-*hydroxy*-8-*methoxychroman*-4-*carboxylate*, m.p. 85° (*Ac* derivative, m.p. 94°), hydrolysed to the *acid*, m.p. 197° (decomp.), which with $Ac_2O$ and $C_5H_5N$ gives 8-*methoxy*-Δ³-*chromene*-4-*carboxylic acid*, m.p. 170°. 5-*Methoxyphenoxyacetic*-2-*acetic acid*, m.p. 163°, obtained by oxidation of the pyruvic acid, gives an *Et* ester, b.p. 178—180°/1 mm., m.p. 37°, which is cyclised to *Et* 3-*hydroxy*-7-*methoxy*-Δ³-*chromene*-4-*carboxylate* (II), m.p. 62—63° (*Ac* derivative, m.p. 51°). This acetate is reduced to 7-*methoxychroman*-4-*carboxylic acid*, m.p. 78°, whilst (II) is hydrogenated to *Et* 3-*hydroxy*-7-*methoxychroman*-4-*carboxylate*, m.p. 97°, hydrolysed to 7-*methoxy*-Δ³-*chromene*-4-*carboxylic acid*, m.p. 131°. The course of the reduction of enol acetates is discussed. F. R. S.

**Reduction experiments with 2 : 3 : 4 : 5-tetraphenylthiophen.** E. Bergmann (J.C.S., 1936, 505).—Reduction (Na–amyl alcohol) of tetraphenylthiophen gives αβγδ-tetraphenylbutane, m.p. 86°, and 1 : 2-diphenyl-3-benzylhydrindene, m.p. 182°, but no reduction occurs with Zn–HCl (cf. Fromm and Achert, A., 1903, i, 340). F. R. S.

**Hydroxypyrrole nitrones. II.** A. H. Blatt (J. Amer. Chem. Soc., 1936, 58, 590—594).—When 2-hydroxy-2 : 3 : 5-triphenylpyrrolenine nitrone (I), m.p. about 180° (decomp.) (prep. A., 1935, 355, whereby a little of a N-free *substance*, m.p. 204°, is also formed), is dissolved in aq. 5% NaOH and the solution acidified with AcOH, the oxime (II), m.p. about 180° (decomp.), of αβ-dibenzoyl-α-phenylethylene (*loc. cit.*) is pptd. ; acidification with HCl or HBr gives (I). (II) is best converted into (I) by a little HCl in $COMe_2$. Methylation (MeI, MeOH–NaOMe) of (II) affords the Me ether (III) (*loc. cit.*) of (I) ; with $Me_2SO_4$ and aq. NaOH, (III) (formation favoured by low alkali concn. and rise of temp.) and the *Me ether*, m.p. 121°, of (II) result. (I) and $Ac_2O$ at 80° give 1 : 4-*diacetoxy*-2 : 3 : 5-*triphenylpyrrole* (IV), m.p.

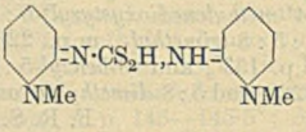
151°, reduced (Zn dust, AcOH, little $CuSO_4$) to 4-*acetoxy*-2 : 3 : 5-*triphenylpyrrole*, m.p. 188°, and thence (red P, I, AcOH) to 2 : 3 : 5-triphenylpyrrole (V). (II) and $Ac_2O$ afford the normal acetate (VI) (*loc. cit.*). The production of (IV) from (I) is explained by the following reactions : (*a*) acetylation of 2-OH, (*b*) addition of $Ac_2O$ to the nitrone system, (*c*) migration of OAc from C2 to C4, (*d*) loss of AcOH between C4 and C5. (I), (II), or (VI) and AcCl give diacethydroxamic acid, 4-chloro-2 : 3 : 5-triphenylfuran, and (mainly) 4-*chloro*-1-*acetoxy*-2 : 3 : 5-*triphenylpyrrole*, m.p. 152°, which is reduced (Zn dust, AcOH, traces of $CuSO_4$, and HCl) to 4-*chloro*-2 : 3 : 5-*triphenylpyrrole*, m.p. 140—141°, and thence (P, HI) to (V). H. B.

**Extension of Michael's reaction. V.** T. N. Ghosh (J. Indian Chem. Soc., 1935, **12**, 692—698; cf. A., 1934, 1010).—αα′-$Et_2$ acetonetetracarboxylic dianilide (I) with boiling AcOH–$Ac_2O$ gives $Et_2$ 2 : 4-*diphenylcarbamido*cyclo*butanone*-2 : 4-*carboxylate*, m.p. 248° (decomp.) (*semicarbazone*, m.p. > 270°). Similarly, (I) with MeCHO, *o*-OMe·$C_6H_4$·CHO, and CHPh:CH·CHO, respectively, instead of $CH_2O$, gives $Et_2$ 2 : 4-*diphenylcarbamido*-3-*methyl*-, m.p. 200—202° (decomp.), -3-*o*-*anisyl*-, m.p. 205—206°, and -3-β-*phenylvinyl*-, m.p. 249—250° (decomp.), -cyclo*butanone*-2 : 4-*dicarboxylate*. (I) with COMePh–$Ac_2O$ (reflux; 2 hr.) gives traces of two *compounds*, m.p. 224—225° (decomp.) and 303—304° (decomp.), the former being sol. and the latter insol. in alkali. $CO(CH_2·CO_2Et)_2$ (II) when treated in $Et_2O$ successively with Na and α-$C_{10}H_7$·NCO (III) gives 3-*carbethoxy*-2 : 4 : 6-*triketo*-1-α-*naphthylpiperidine* (IV), m.p. 191—192° (decomp.) (*Na* salt), also obtained directly from (II) and (III), and hydrolysed to 2 : 4 : 6-*triketo*-1-α-*naphthylpiperidine* (V), m.p. 249—250° (decomp.). (IV) when refluxed with CHPh:CH·CHO or with *o*-$NO_2$·$C_6H_4$·CHO yields, respectively, 3-*carbethoxy*-2 : 4 : 6-*triketo*-1-α-*naphthyl*-3 : 5-*cinnamylidene*-, m.p. 236—237° (decomp.), and -3 : 5-*o*-*nitrobenzylidene*-, m.p. > 300°, -*piperidine*. Similarly, 2 : 4 : 6-*triketo*-α-*naphthyl*-3 : 5-*cinnamylidene*-, m.p. 263—264°, and -3 : 5-*o*-*nitrobenzylidene*-, m.p. 233—235°, -*piperidine*, both insol. in alkali, were prepared from (V). (II) when treated in abs. $Et_2O$ successively with Na and carbethoxythiocarbimide in PhMe yields $Et_2$ 2 : 6-*dicarbethoxyiminothiopyran*-4-*one*-3 : 5-*dicarboxylate*, m.p. 122—123°. The ring structure is proved by the absence of mercaptan properties and stability to HgO. The $Na_2$-derivative of Et 2 : 6-diketo-4 : 4-dimethylcyclohexane-3 : 5-dicarboxylate does not react with PhNCO. H. G. M.

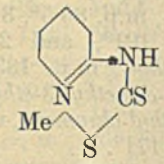
**Production of piperidine derivatives.**—See B., 1936, 476.

**Syntheses in the pyridine series.** A. E. Tschitschibabin (Bull. Soc. chim., 1936, [v], 3, 762—779).—A lecture.

**Action of carbon disulphide on methylpyridonimine.** K. S. Topschiev (Compt. rend. Acad. Sci. U.R.S.S., 1936, 1, 23—26).—Methylpyridonimine (prepared from 2-$C_5H_4N·NH_2$ and MeI) with $CS_2$–EtOH gives the *methylpyridonimine* salt (I), m.p. 160°, of N-*methylpyridinedithiocarbamic acid*, but with $CS_2$ alone gives N-*methylpyridodithiodiazole* (II), m.p. 135°, b.p. 173°/3 mm. without decomp., sparingly sol. in $H_2O$ and unaffected by conc. aq. NaOH.



(I.)



(II.)

H. G. M

**β-(2-Pyridyl)alanine.** J. Overhoff, J. Boeke, and A. Gorter (Rec. trav. chim., 1936, **55**, 293—296).—ω-(2-Pyridyl)methylamine [from 2-cyanopyridine and $Cr(OAc)_2$] is converted by $NaNO_2$–HCl into *chloro*-(2-*pyridyl*)*methane*, b.p. 73—76°/10 mm. (*picrate*, m.p. 152—153°); interaction with $C_6H_4(CO)_2N·CNa(CO_2Et)_2$ then affords $Et_2$ α-(2-*pyridyl*)-β-*phthalimidoethane*-ββ-*dicarboxylate*, m.p. 120°, hydrolysed by HCl to β-(2-*pyridyl*)*alanine dihydrochloride* (I), m.p. 209—210°; (I) with 2 equivs. of $Ag_2O$ affords β-(2-*pyridyl*)*alanine*, m.p. 216—217° (decomp.). {*Picrate* [from (I) and $OH·C_6H_2(NO_2)_3$], m.p. 164—165°; *monohydrochloride* [from (I) and 1 equiv. of $Ag_2O$], m.p. 190—191°.} P. G. C.

**Nitration method of 8-nitro-6-methoxyquinoline.** K. S. Topschiev (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 263—264).—Addition of $HNO_3$–$H_2SO_4$ to 8-nitro-6-methoxyquinoline in $H_2SO_4$ below 40° gives 5 : 8-*dinitro*-6-*methoxyquinoline*, m.p. 234°, in good yield. H. G. M.

**Cases of mobility of the nitro-group. Mobility of the nitro-group in 5 : 8-dinitro-6-methoxyquinoline.** K. S. Topschiev (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 264—266; cf. preceding abstract).—5 : 8-Dinitro-6-methoxyquinoline when heated with δ-amino-α-diethylaminopentane gives 5-*nitro*-8-(δ-*diethylamino*-α-*methylbutyl*)*amino*-6-*methoxyquinoline*, reduced by $SnCl_2$–HCl to the corresponding 5-$NH_2$-derivative, b.p. 250°/3 mm., which gives a *salt*, m.p. 165°, with 1 mol. of di-(2-hydroxy-3-carboxynaphthyl)methane. This salt is also obtained by similar methods from the nitration product of 8-(δ-diethylamino-α-methylbutyl)amino-6-methoxyquinoline. H. G. M.

**Changes of "colour" which accompany the conversion of amino-acids and amides into lactams in the benzene series.** (Mme.) Ramart-Lucas and (Mlle.) Biquard (Bull. Soc. chim., 1935, [v], 2, 1383—1388).—The ultra-violet absorption spectra of Na *o*-aminophenyl-acetate and -propionate closely resemble that of *o*-$C_6H_4Me·NH_2$. Cyclisation of the side-chain affects the spectra (1) by altering the nature of the chromophores, and (2) by the true effect of cyclisation. The absorption spectra of the corresponding cyclic compounds oxindole and its *N*-Me and 1 : 3 : 3-$Me_3$ (I) derivatives are closely similar, as are also the spectra of 2-keto-1 : 2 : 3 : 4-tetrahydroquinoline and its 1-Me and 1 : 4-$Me_2$ (II) derivatives. All these, therefore, have a lactam structure, and conversion of an $NH_2$-acid into the lactam is accompanied by a hypsochromic effect. Comparison of the spectra of *o*-$C_6H_4Me·NMe·CO·CMe_2Bu^a$ with those of (I) and (II) shows that the true effect of cyclisation is a bathochromic one. J. W. B.

**Synthesis of Plasmocide [8-(γ-*N*-diethylaminopropyl)amino-6-methoxyquinoline methylene bis-salicylate].** O. J. Magidson, I. T. Strukov, M. D. Bobischev, and S. F. Torf (J. Appl. Chem. Russ., 1936, **9**, 304—321).—8-Amino-6-methoxyquinoline (I) is prepared on the industrial scale by the steps: *p*-$C_6H_4Cl\cdot NO_2$ → *p*-$NO_2\cdot C_6H_4\cdot OMe$ → *p*-$NH_2\cdot C_6H_4\cdot OMe$ → *p*-$NHAc\cdot C_6H_4\cdot OMe$ → *m*-nitro-*p*-anisidine → 8-nitro-6-methoxyquinoline → (I). $NEt_2\cdot[CH_2]_3Cl$ (II) was obtained as follows: glycerol → diformin → allyl formate → $CH_2{:}CH\cdot CH_2Cl$ → $CH_2Cl\cdot CH_2\cdot CH_2Br$ → (II). (I) and (II) are condensed to yield 8-(γ-*N*-diethylaminopropyl)amino-6-methoxyquinoline, the methylene bis-salicylate of which has marked plasmocidal properties. R. T.

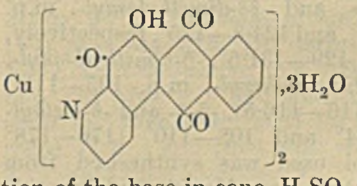
**Syntheses in the 2-phenylquinoline series. I. Synthesis of bromine-substituted 2-phenylquinoline-4-carboxylic acids. Reactivity of the bromine therein. Curtius degradation of 6- and 4′-bromoatophan.** K. Feist and M. Kuklinski (Arch. Pharm., 1936, **274**, 244—255).—5-Bromoisatin, COPhMe, and 33% KOH at 100° give 6-*bromo-2-phenylquinoline-4-carboxylic acid* (I), m.p. 239·5°, which affords successively the *Et* ester, m.p. 97·5°, *hydrazide*, +EtOH, m.p. 226° [*benzylidene*, m.p. 271°, and *salicylidene* derivative, +2EtOH (lost only slowly at 130°), double m.p. 153° and 237°], *azide*, m.p. 113°, and *urethane*, m.p. 192°, and 6-*bromo-4-amino-2-phenylquinoline*, m.p. 209° (*hydrochloride*, m.p. 328°; *$Ac_2$* derivative, m.p. 166°). Isatin and *p*-$C_6H_4Br\cdot COMe$, m.p. 53·5°, afford similarly 2-p-*bromophenylquinoline-4-carboxylic acid* (II), m.p. 241°, the *Et* ester, m.p. 95°, *hydrazide*, m.p. 247·5° (*benzylidene*, +EtOH, m.p. 245°, and *salicylidene* derivative, m.p. 274°), *azide*, m.p. 96°, and *urethane*, m.p. 154°, and 4-*amino*-2-p-*bromophenylquinoline*, m.p. 164° (*hydrochloride*, m.p. 326°; *$Ac_2$* derivative, m.p. 231·5°). The Br in (I) is unreactive, since with $NH_2Me$ in EtOH at 200° it affords only the *methylamide*, m.p. 244°, hydrolysed to (I) by alkali. Further, activated Mg does not react with (I), (II), 4-bromo-2-phenylquinoline, or *Et* 3-*bromo-2-phenylquinoline-4-carboxylate*, m.p. 88·5°. The prep. of 3-bromo-2-phenylquinoline-4-carboxylic acid, m.p. 236° (lit. 231°), is improved. R. S. C.

**Acridones. VII. Acridol, a tautomeric form of acridone.** I. Tanasescu and E. Ramontianu (Bull. Soc. chim., 1935, [v], **2**, 1485—1488).—The red substance, m.p. 350°, obtained from 5-chloroacridine in boiling $PhNO_2$ (Marzin, A., 1933, 1059, where the m.p. 250° is an error) is really acridone, m.p. 354°, and not 5-hydroxyacridine, the colouring matter being an impurity. J. W. B.

**Meso-derivatives of acridine. IV. 9-Phenoxyacridines. V. Derivatives of 9-aminoacridine.** N. S. Drozdov and O. M. Tscherntzov (J. Gen. Chem. Russ., 1935, **5**, 1576—1580, 1736—1743).—IV. 5-Chloroacridine and PhOH at 100° yield the hydrochloride of 5 : 5-diphenoxy-5 : 10-dihydroacridine, converted by aq. $NH_3$ into 5-phenoxyacridine (I), m.p. 125—126° (lit. 112°). The following derivatives of (I) have been prepared analogously: 5-*phenoxy-3-methoxy-* (II), m.p. 151—152° (*hydrochloride*, m.p. 222—225°), 2-*chloro-*, m.p. 169—170°, and 3-*nitro-5-phenoxy-7-methoxy-acridine* (III), m.p. 173°, 2-*chloro-*, m.p. 191—194°, and 3-*nitro-5 : 5-diphenoxy-7-methoxy-5 : 10-dihydroacridine hydrochloride*, m.p. 173°. The above substances are converted into the corresponding acridones by boiling with dil. acids.

V. 5-Aminoacridine (IV) is obtained in theoretical yield by adding $NH_4Cl$ to (I) in fused PhOH at 100°, and treating the hydrochloride of (IV) so obtained with aq. $NH_3$. The following derivatives of (IV) are obtained analogously: from (II) and $NH_4Cl$, $NH_2Me,HCl$, or $NH_2Ph,HCl$, 5-*amino-*, m.p. 231°, 5-*methylamino-*, m.p. 176° (*hydrochloride*, $+2H_2O$, m.p. 272—275°), and 5-*anilino-3-methoxyacridine*, m.p. 202—203° (*hydrochloride*, m.p. 262—266°); from 3 : 5-dichloro-7-methoxyacridine, PhOH, and γ-piperidino-β-hydroxypropylamine, 1-phenyl-2 : 3-dimethyl-5-pyrazolone, or *p*-anisidine, 3-*chloro-5-(γ-piperidino-β-hydroxypropyl)amino-* (*hydrochloride*, m.p. 105—110°), 3-*chloro-5-(1′-phenyl-2′ : 3′-dimethyl-5′-pyrazolonyl)-* (*hydrochloride*, m.p. 250°), or 3-*chloro*-p-*anisidino-7-methoxyacridine*, m.p. 203—204° [*hydrochloride*, m.p. 277—278° (decomp.)]; from (III) and $NHPh_2$ or *p*-anisidine hydrochloride, 3-*nitro-5-anilino-*, m.p. 224° (+*EtOH*, decomp. 105—110°), and 3-*nitro*-5-p-*anisidino-7-methoxyacridine*, m.p. 212—213°. 5-*Piperidino-3-methoxyacridine*, m.p. 102—103°, is prepared by heating (II) with PhOH and piperidine at 100°. R. T.

**Copper lake of alizarin-blue base (1 : 2-dihydroxyanthraquinone-3-quinoline).** I. Chmelnitzkaja, M. Korovin, and E. Goldman (Anilinokras. Prom., 1935, **5**, 135—137).—The salt of annexed constitution is pptd. when a solution of the base in conc. $H_2SO_4$ is added to aq. $CuSO_4$. R. T.



**Isomerisation of saturated and unsaturated hydantoins.** D. A. Hahn and M. K. Seikel (J. Amer. Chem. Soc., 1936, **58**, 647—649).—Successive treatment of 5-benzylidene-3-methylhydantoin with EtOH–NaOEt and $CHPhBr\cdot CO_2Et$ gives *Et 5-benzylidene-3-methylhydantoin-1-phenylacetate* (I), m.p. 134—135°; an *isomeride* (II), m.p. 106·5—107·5°, is obtained from (VI) or (VIII), below, and EtOH—HCl. Hydrolysis (aq. EtOH–NaOH) of (I) affords the *Na* salts, m.p. 288° (decomp.) (III) and 217° (decomp.) (IV) [corresponding *Ba* salts, m.p. 213—215° (decomp.) (V) and 312—320° (decomp.) (VI)], of two forms of 5-*benzylidene-3-methylhydantoin-1-phenylacetic acid*, m.p. 186—187° (VII) and 170° (VIII). The various pairs in the series (I)—(VIII) are geometrical isomerides. Reduction [red P and HI (*d* 1·7) at 105—110°] of (I), (VII), or (VIII) gives 5-*benzyl-3-methylhydantoin-1-phenylacetic acid* ($+H_2O$) (IX), m.p. (anhyd.) 147—147·5°; an *isomeride* (X), m.p. 129—131°, is obtained by acidification of (XIV) and (XVI) (below). Crude (IX) and EtOH–HCl afford isomeric *Et* esters, m.p. 123·5—124·5° (XI) and 60—61·5° (XII), which are hydrolysed (aq. EtOH–NaOH) to the corresponding *Na* salts, m.p. 156—157° (XIII) and 293—295° (XIV) [corresponding *Ba* salts, m.p. 284° (decomp.) (XV) and 300—307° (decomp.) (XVI)], of (IX) and (X), respectively.

The various pairs of (IX)—(XVI) are stereoisomeric forms. (IX) is hydrolysed by aq. $Ba(OH)_2$ to β-phenylalanine-*N*-phenylacetic acid. H. B.

**Relation of structure of dialkylbarbituric acids to length of their [anæsthetic] action.** H. A. Shonle, J. H. Waldo, A. K. Keltch, and H. W. Coles (J. Amer. Chem. Soc., 1936, **58**, 585—587).—The appropriate bromide and $CNaEt(CO_2Et)_2$ in EtOH give *Et ethyl*-αδ-, -αγ-, and -βδ-*dimethylamyl*-, b.p. 133—134°/7·5 mm., 126—127°/4 mm., and 140—141°/10 mm., respectively, -α-*propylbutyl*-, b.p. 110—111°/3 mm., -δ-*methylheptyl*-, b.p. 115—116°/1 mm., -βδ-*dimethylhexyl*-, b.p. 107—109°/1 mm., -β-*ethylhexyl*-, b.p. 127—130°/4 mm., -β- and -δ-*methylamyl*-, b.p. 103—105°/2 mm. and 108°/2 mm., respectively, -γ- and -ε-*methyl*-β-*ethylhexyl*-, b.p. 120—123°/2·5 mm. and 125—128°/1 mm., respectively, -αγ-*dimethylbutyl*-, b.p. 97·5—99°/3 mm., and -β-*ethylbutyl*-, b.p. 167°/30 mm., -*malonates*. The following *bromides* (primary prepared with $PBr_3$ or HBr–conc. $H_2SO_4$; *sec.* usually obtained with dry HBr) are new: αδ-, αγ-, and βδ-*dimethylamyl*, b.p. 67—72°/40 mm., 67—71°/40 mm., 65—66°/27 mm., respectively, δ-*methylheptyl*, b.p. 73—74°/16 mm., βδ-*dimethylhexyl*, b.p. 76—81°/22 mm., β-*ethylhexyl*, b.p. 93—98°/40 mm., and γ- and ε-*methyl*-β-*ethylhexyl*, b.p. 88—92°/20 mm. and 84—92°/20 mm., respectively. The above malonates and $CO(NH_2)_2$ in EtOH–NaOEt give 5-*ethyl*-5-αδ-, -αγ-, and -βδ-*dimethylamyl*-, m.p. 136—136·6°, 126—127°, and 124·8—125°, respectively, -5-α-*propylbutyl*-, m.p. 129—131·5°, -5-δ-*methylheptyl*-, m.p. 77—79°, -5-βδ-*dimethylhexyl*-, m.p. 105—115°, -5-β-*ethylhexyl*-, m.p. 116—116·5°, -5-β- and -δ-*methylamyl*-, m.p. 151—154° and 108—110° [176—178° when original alcohol used was synthesised from $MgBu^{\beta}Br$ and $(CH_2)_2O$ or from Mg *iso*amyl bromide and $CH_2O$], respectively, -5-γ- and -ε-*methyl*-β-*hexyl*-, m.p. 150—152° and 134·8—135·6°, respectively, -5-αγ-*dimethylbutyl*-, m.p. 173·5—174·5°, and -5-β-ethylbutyl-, m.p. 134—134·5° (lit. 125°), -*barbituric acids*. Some of these acids are also prepared from $CN{\cdot}CEtR{\cdot}CO_2Et$; the esters with R = βδ-dimethylamyl, b.p. 128°/3—4 mm., α-propylbutyl, b.p. 131°/2—3 mm., and β-ethylhexyl, b.p. 152—153°/4 mm., are described. Et α-propylbutylcyanoacetate has b.p. 123—125°/3 mm. Pharmacological data for the acids are given; the duration of anæsthetic action bears no direct relationship to the amount of acid required to produce anæsthesia or to the mol. wt. of the complex alkyl group. H. B.

**Preparation of a barbituric acid and salts thereof.**—See B., 1936, 395.

**Ferric complexes of antipyrine.** J. V. Dubský, E. Krametz, and J. Trtílek (Coll. Czech. Chem. Comm., 1936, **8**, 141—148; cf. A., 1935, 1252).—Dark brown $[Fe(CN)_5NO_2]Fe,4B,4H_2O$ ($B$ = antipyrine), decomp. 110°, is pptd. by addition of cold aq. $FeCl_3$ to $[Fe(CN)_5NO_2]Na_3$ and antipyrine, whilst greyish-brown $[Fe(CN)_5NO_2]_2Fe_2,3B$ may be similarly obtained from $[Fe(CN)_5NO_2]K_3$. $[Fe(CN)_5NO_2]Na_4$ gives a compound of the Prussian-blue type with $FeCl_3$ whilst $[Fe(CN)_5NH_3]Na_3$ yields greenish-blue $[Fe(CN)_5NH_3]Fe,8H_2O$. The *compounds* $[Fe(CN)_5NH_3]_3Fe_2,3B$, $[Fe(CN)_6]Fe,3B,8H_2O$, and $[Cr(SCN)_6]Fe,3B,8H_2O$ have also been prepared. R. S.

**Glucosides of the glyoxaline series.** E. Bergmann and H. Heimhold (J.C.S., 1936, 505—506).—Ag glyoxaline with tetra-acetobromoglucose gives *tetra-acetoglucosidoglyoxaline*, m.p. 205—208°, deacetylated to *glucosidoglyoxaline*, m.p. 217°; similarly *triacetorhamnosidoglyoxaline*, m.p. 177—179°, is deacetylated to *rhamnosidoglyoxaline*, m.p. 153—156°. F. R. S.

**Action of isatin on α-naphthyl ethyl ether.** C. Marschalk (Bull. Soc. chim., 1936, [v], 3, [A], 124—129, [B], 129—134).—[A] 4 : 4′-Diethoxy-1 : 1′-dinaphthyl (I) is formed from $\alpha$-$C_{10}H_7{\cdot}OEt$ (II) and isatin with cold 83% $H_2SO_4$, but not with conc. $H_2SO_4$ when other *products*, one (III) of which is insol. in cold $H_2O$, alkalis, and boiling PhMe, are formed (cf. A., 1927, 673). The formation of (I) is probably due to the interaction of excess of (II) with (III), and not to oxidation by $H_2SO_4$. The reaction is analogous to that previously described (this vol., 721). Isatin (III) itself, however, does not act as the H-acceptor. (I) is also obtained when (II) is treated with phenanthraquinone and $H_2SO_4$ in the cold.

[B] (II), (III), and 93·5% $H_2SO_4$ give a *compound*, m.p. 255—256° when carefully purified, identical with 3-(4′-*ethoxy*-1′-*naphthyl*)*dioxindole*, obtained from $OEt{\cdot}C_{10}H_6{\cdot}MgBr$ and (III). This with (II) and 84% $H_2SO_4$ gives (I) and a *compound*, m.p. 214—215°, also obtained in the reaction between (II), (III), and 84% $H_2SO_4$. The formation of (I) requires 3 mols. of (II) for one of (III). H. G. M.

**Complex salts of dipyridyl with bivalent and tervalent cobalt.**—See this vol., 692.

**Quinazolines. XLI. Synthesis of some new 4-quinazoline derivatives from *p*-bromoaniline, formaldehyde, and hydrochloric acid.** S. E. Cairncross and M. T. Bogert (Coll. Czech. Chem. Comm., 1935, 7, 548—554).—6-*Bromo*-3-p-*bromophenyl*-4-*quinazolone* (I), m.p. 257°, but not the expected quinazoline, is formed together with two other *bases*, m.p. 204° and 193—196°, when $p$-$C_6H_4Br{\cdot}NH_2$ is heated (70°, 1 hr.) with $HCl$–$H_2SO_4$–$H_2O$ and $CH_2O$, methylal, or $CH_2Cl_2$, and is also obtained when 5-bromoanthranilic acid and $p$-$C_6H_4Br{\cdot}NH{\cdot}CHO$ are heated in an evacuated flask (2 hr.). It is unaffected when heated with $H_2SO_4$ at 60°, $HCO_2H$–$H_2SO_4$, $Ac_2O$, AcCl–NaOAc, $KMnO_4$ at 70°, or by $HNO_2$, but is reduced (Pd–$CaCO_3$, $H_2$ 19 lb. per sq. in.) to 3-phenyl-4-quinazolone, also obtained by heating anthranilic acid with $NHPh{\cdot}CHO$. (I) when heated (sealed vessel, 6 hr., 85—90°) with $N_2H_4,H_2O$ in EtOH yields 6-*bromo*-3-*amino*-4-*quinazolone*, m.p. 227—228·2°, reduced (Pd–$CaCO_3$–$H_2$) to 3-*amino*-4-*quinazolone*, m.p. 210—211°, which when diazotised and coupled with $\beta$-$C_{10}H_7{\cdot}OH$ gives a reddish-brown dye, and is also obtained on heating 3-phenyl-4-quinazolone with $N_2H_4,H_2O$ (cf. Paal *et al.*, who considered the product to be a hydrazone; A., 1890, 71). H. G. M.

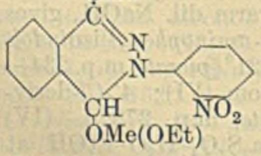
**Imidochlorides. III. Reaction of anilide imidochlorides and ethyl sodiomalonate.** R. C.

Shah and V. R. Heeramaneck. **IV. Condensation of anilide imidochlorides with urethanes. New synthesis of 4-hydroxy-2-phenylquinazolines.** R. C. Shah and M. B. Ichaporia (J.C.S., 1936, 428—430, 431—432).—III. Condensation of anilide imidochlorides with $CH_2(CO_2Et)_2$ and its Na derivative in PhMe gives chiefly mono- and little di-condensation products; the mono-condensation products are cyclised to the corresponding quinolines. *p*-$C_6H_4Me{\cdot}NH_2$ and Et (anilobenzyl)malonate (I) afford *(anilobenzyl)malonodi*-p-*toluidide*, m.p. 208—210°, or on further heating the p-*toluidide* of *4-hydroxy-2-phenylquinoline-3-carboxylic acid*, m.p. 255—257°. (I) with BzCl and Na yields *Et benzoyl(anilobenzyl)-malonate*, m.p. 156—158°. The following have been similarly prepared: *Et (anilo*-p-*nitrobenzyl)malonate*, m.p. 101°, *Et 4-hydroxy-2*-(p-*nitrophenyl)quinoline-3-carboxylate*, m.p. 239—241°, and the *carboxylic acid*, m.p. 197—199° (efferv.); *Et (anilo*-o-*chlorobenzyl)-malonate*, m.p. 77°, *Et 4-hydroxy-2*-o-*chlorophenylquinoline-3-carboxylate*, m.p. 239—242°, and the *carboxylic acid*, m.p. 242—244°; *Et* (p-*nitroanilobenzyl)malonate*, m.p. 103°, *Et 6-nitro-4-hydroxy-2-phenylquinoline-3-carboxylate*, m.p. >300°, and the *carboxylic acid*, m.p. 295—297°; *4-hydroxy-2-phenyl-8-methylquinoline-3-carboxylic acid*, m.p. 201—203° (decomp.); *Et* (m-, m.p. 67—68°, and *Et* (p-*tolyliminobenzyl)malonate*, m.p. 62—63°, *Et 4-hydroxy-2-phenyl*-(5 or 7)-, m.p. 237—240°, and -(7 or 5)-*methylquinoline-3-carboxylate*, m.p. 225—228°, *4-hydroxy-2-phenyl-6-methylquinoline-3-carboxylic acid*, m.p. 209—211° (decomp.); *benzo*-o-*chloroanilide imidochloride*, b.p. 214—215°/40 mm., o′-*chlorophenylbenzamidine*, m.p. 113—114° (*hydrochloride*, m.p. 219—220°); *Et* (o-*chloroanilobenzyl)malonate*, m.p. 104—105°, *Et 8-chloro-4-hydroxy-2-phenylquinoline-3-carboxylate*, m.p. 155—156°, and the *carboxylic acid*, m.p. 184—186°; *benzo*-m-*chloroanilide imidochloride*, b.p. 229—231°/50 mm., m-*chlorophenylbenzamidine*, m.p. 123—124° (*hydrochloride*, m.p. 233—235°; *Et* (5 or 7)-*chloro-4-hydroxy-2-phenylquinoline-3-carboxylate*, m.p. 234—237°; *Et* (p-*chloroanilobenzyl)malonate*, m.p. 75°, *Et 6-chloro-4-hydroxy-2-phenylquinoline-3-carboxylate*, m.p. 251—252°, and the *carboxylic acid*, m.p. 300°.

IV. Benzanilide imidochloride and the Na derivative of urethane condense to *(anilobenzyl)urethane* (*hydrochloride*, m.p. 215—217°), which with α-$C_{10}H_7{\cdot}NH_2$ forms s-*(anilobenzyl)-α-naphthylcarbamide*, m.p. 258—260°. (I) similarly condenses with Me carbamate to *Me (anilobenzyl)carbamate*, and with acetylurethane to *acetyl(anilobenzyl)urethane*, m.p. 85—88°, cyclised to *3-acetyl-2-phenyl-4-quinazolone*, m.p. 233°. Benzo-α-naphthalide imidochloride and urethane afford *(α-naphthyliminobenzyl)urethane*, cyclised to *4-hydroxy-2-phenyl*-1 : 3-*naphtha*iso*diazine*, m.p. 300°; (β-naphthyliminobenzyl)urethane, cyclised to *4-hydroxy-2-phenyl-2 : 4-naphtha*iso*diazine*, m.p. 295—298°, is similarly obtained.

F. R. S.

**A reaction of certain diazosulphonates derived from β-naphthol-1-sulphonic acid. XIII. Fission of the naphthalene nucleus and subsequent closure in two directions.** F. M. Rowe, W. C. Dovey, B. Garforth, E. Levin, J. D. Pask, and A. T. Peters. **XIV. Preparation of 1 : 4-diketo-3-(nitroaryl)tetrahydrophthalazines or 4-keto-1-hydroxy-3-(nitroaryl)-3 : 4-dihydrophthalazines and related compounds.** F. M. Rowe, J. G. Gillan, and A. T. Peters (J.C.S., 1935, 1796—1808, 1808—1815; cf. A., 1935, 1253).—XIII. 2 : 1-$OH{\cdot}C_{10}H_6{\cdot}SO_3Na$ and diazotised *o*-nitroaniline give 2′-nitrobenzene-β-naphthol-1-diazosulphonate, which dissolves in aq. $Na_2CO_3$ giving Na 1-(2′-nitrobenzeneazo)-β-naphthaquinone-1-sulphonate (I). This when treated with cold conc. NaOH and then HCl gives *Na benzaldehyde-2′-nitrophenylhydrazone-ω-sulphonate-2-β-acrylic acid* (II) (the corresponding 4′- and 5′-*chloro-2′-nitro*-compounds were similarly prepared), which when boiled with HCl (8 hr.) yields *benzo-2′-nitrophenylhydrazide-2-β-acrylic acid* (III), m.p. 220—225° (4′-*Cl*-derivative, m.p. 272—278°), and 2-(2′-*nitrophenylamino*)iso*indolinone-3-acetic acid* (IV), m.p. 224—225° [*Me*, m.p. 164°, and *Et* ester, m.p. 153°; *anilide*, m.p. 272°; 4′-*Cl*-derivative, m.p. 278° (*Me* ester, m.p. 152°; *anilide*, m.p. 268°); 5′-*Cl*-derivative, m.p. 248° (*Me*, m.p. 182°, and *Et* ester, m.p. 184°)], obtained when (III) melts, or is boiled with $PhNO_2$ or aq. $Na_2CO_3$ (a similar interconversion occurs also with the 4′-*Cl*-derivatives). (IV) [or (III)] when refluxed with $Ac_2O$, or better with $Ac_2O$–$C_5H_5N$ (3 hr.), or with $PCl_3$–PhMe (2 hr.) yields 2 : 5-*diketo*-3-(2′-*nitrophenyl*)-iso*indolinopyrazolidocoline* (V), m.p. 209° (4′-, m.p. 248—249°, and 5′-Cl-derivatives, m.p. 209°), hydrolysed to (IV) and reduced by Fe–AcOH–$H_2O$ to 2 : 5-*diketo*-3-(2′-*aminophenyl*)iso*indolinopyrazolidocoline* (VI), m.p. 234—236° [*Ac* derivative (VII), m.p. 175—176°; 4′-*Cl*-derivative, m.p. 253—254° (*Ac* derivative, m.p. 242—243°)]. This when treated (*a*) with $H_2SO_4$ at 70° and then with NaOH, (*b*) with $PCl_3$–PhMe under reflux (2 hr.) and then with warm dil. NaOH, gives 2 : 2′-*anhydro*-2 : 5-*diketo*-3-(2′-*aminophenyl*)iso*indolinopyrazolidocoline*, m.p. 219—221° [*picrate*, m.p. 234—236°, also obtained directly from (VI); 4′-*Cl*-derivative, m.p. 238—239° (*sulphate*, m.p. 278°)]. (IV) when treated with NaOH–$Na_2S_2O_4$–$H_2O$–EtOH at 70°, or with $SnCl_2$, is reduced to 2-(2′-*aminophenylamino*)iso*indolinone-3-acetic acid*, m.p. 182—183° (decomp.) [4′-*Cl*-derivative, m.p. 195° (decomp.)], converted by $Ac_2O$ or $Ac_2O$–$C_5H_5N$ into (VII), and when refluxed with $H_2SO_4$ into 2-(2′-*aminophenylamino*)iso*indolinone-3-acetic acid lactam*, m.p. 227° (*hydrobromide*, m.p. 264—265°; *picrate*, m.p. 229—230°; 4′-*Cl*-derivative, m.p. 237°). (I) and (II) when kept with NaOH each yield *Na H* 3-(2′-*nitrophenyl*)-3 : 4-*dihydrophthalazine-1-sulphonate-4-acetate* [4′- and 5′- (impure) -*Cl*-derivatives], converted by boiling $H_2O$–HCl into 1-*hydroxy*-3-(2′-*nitrophenyl*)-3 : 4-*dihydrophthalazine-4-acetic acid* (VIII), m.p. 248° [*Me*, m.p. 146°, and *Et* ester, m.p. 163°; *anilide*, m.p. 128°; 4′-*Cl*-derivative, m.p. 229—230° (*Me*, m.p. 163—164°, and *Et* ester, m.p. 145°; *anilide*, m.p. 130°); 5′-*Cl*-derivative, m.p. 241—242° (*Me*, m.p. 163°, and *Et* ester, m.p. 153°; *anilide*, m.p. 223°)]. The N-*Me ether* [1-*keto*-3-(2′-*nitrophenyl*)-2-*methyltetrahydrophthalazine-4-acetic acid*] has m.p. 207° [*Me* ester, m.p. 133—134°; 4′-*Cl*-derivative, m.p. 207° (*Me* ester, m.p. 129—130°); 5′-*Cl*-derivative, m.p. 225° (*Me* ester, m.p. 143°)]. (VIII) is reduced by boiling AcOH–$H_2O$–Fe (5 min.) to 1-*keto*-3-(2′-*aminophenyl*)-2-*methyltetrahydrophthalazine-4-acetic acid* [*lactam*, m.p. 315—317°; 4′-*Cl*-derivative, m.p. 225°, resolidifying and melting again at 300° (decomp.) (*lactam*, m.p. 321°)], and by boiling AcOH–$H_2O$–Fe (10 min.), or by $SnCl_2$, to 1-*hydroxy*-3-(2′-*aminophenyl*)-3 : 4-*dihydrophthalazine*-4-*acetic acid* (IX), m.p. 160°, resolidifying at 170° and melting again at 293—294° [*lactam*, m.p. 293°; 4′-*Cl*-derivative (X), m.p. 214°, resolidifying at 220°, and remelting at 304° (*lactam*, m.p. 304°); *lactam* of 5′-*Cl*-derivative has m.p. 303—304°]. (VIII) when refluxed with $Ac_2O$–$C_5H_5N$ yields (V); the 4′- and 5′-Cl derivatives of (VIII) undergo a similar conversion. (X) or its lactam when refluxed with dil. $H_2SO_4$ yields 4′-*chloro*-2′-*amino*-3-*phenylphthalaz*-1-*one*, sublimes at 300—350° (*Ac* derivative, m.p. 130—131°). Similar treatment of (IX) gives a *compound*, m.p. 165°, with the expected properties of 2′-amino-3-phenylphthalaz-1-one despite the poor analyses. It is converted by boiling solvents into a colourless *substance*, m.p. >360°, and is reduced by hot $H_2SO_4$–Zn to *o*-benzylenebenziminazole, also obtained from (IX) with $SnCl_2$–conc. HCl and then Sn–HCl. 5-*Chloro*-o-*benzylenebenziminazole* (XI), m.p. 242°, similarly prepared from (X) and also obtained from *o*-$C_6H_4(CHO)_2$, 4 : 1 : 2-$C_6H_3Cl(NH_2)_2$, $H_2O$, and $Na_2CO_3$, is oxidised by $KMnO_4$–AcOH to 5-*chloro*-o-*benzoylenebenziminazole*, m.p. 156°, converted by boiling aq. $Na_2CO_3$ into 5-*chloro*-2-*phenylbenziminazole*-o-*carboxylic acid*, m.p. 285°. (VIII) when refluxed with $H_2SO_4$–$H_2O$ (2 hr.) gives, on neutralisation with NaOH, 2′-*nitro*-3-*phenylphthalaz*-1-*one*, m.p. 266° (*picrate*, m.p. 214—215°), reduced by $Na_2S$–$H_2O$ to an intractable resin, and converted by $Me_2SO_4$–$PhNO_2$ at 110—120° into the *compounds* (XII), m.p. 135° from MeOH, and 150° from EtOH, decomposed by heat but without formation of 4-keto-1-methoxy-3-(2′-nitrophenyl)-3 : 4-dihydrophthalazine. Similarly 4′-*chloro*-2′-*nitro*-3-*phenylphthalaz*-1-*one*, m.p. 233° (similarly prepared), gives methylation *products*, m.p. 138° from MeOH, and 110° from EtOH, decomposed by heat but not to the corresponding 4-keto-compound, and is reduced by $Na_2S$–$H_2O$ to a resin and by Zn–$H_2SO_4$ to (XI). (VIII) when treated with $H_2SO_4$–$H_2O$–$Na_2Cr_2O_7$ gives 2′-*nitro*-3-*phenyl*-4-*methylphthalaz*-1-*one* (XIII), m.p. 226° (decomp.) (*picrate*, m.p. 217°). This and the corresponding 4′-*chloro*-2′-*nitro*-compound (XIV), m.p. 237° (*picrate*, m.p. 233°), are methylated by $Me_2SO_4$, but the products do not have the expected properties. (IX) and (X) or their lactams, when treated with $H_2SO_4$–$H_2O$–$Na_2Cr_2O_7$ give, respectively, 2′-*amino*-, m.p. 302°, and 4′-*chloro*-2′-*amino*-3-*phenylphthalaz*-1-*one*-4-*acetic acid lactam*, m.p. 314°, converted by $Na_2S$–$H_2O$ into the $NH_2$-acid, m.p. 287°, resolidifying and then melting at 314°. The foregoing lactams when treated with boiling $Na_2S$–$H_2O$ or NaOH–$H_2O$ yield 2′-*amino*-, m.p. 218° (*Ac* derivative, m.p. 274°), and 4′-*chloro*-2′-*amino*-3-*phenyl*-4-*methylphthalaz*-1-*one*, m.p. 257° (*Ac* derivative, m.p. 296°), respectively, also obtained from (XIII) and (XIV) with boiling $Na_2S$–$H_2O$, and reduced by $H_2SO_4$–Zn–$H_2O$ to 1-*keto*-3-(2′-*aminophenyl*)-4-*methyltetrahydrophthalazine*, m.p. 221°, and its 4′-*Cl*-derivative, m.p. 200°, respectively, also obtained by a similar reduction of (XIII) and (XIV).

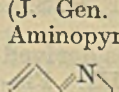


(XII.)

XIV. *p*-$NO_2 \cdot C_6H_4 \cdot NH \cdot NH_2$ (XV) and *o*-$C_6H_4(CO)_2O$ (XVI) in $CHCl_3$ give o-*carboxybenzo*-4′-*nitrophenylhydrazide*, m.p. 241—245°, converted by boiling $PhNO_2$ into phthalyl-4′-nitrophenylhydrazide (A., 1906, i, 588), also obtained when (XV) and (XVI) are heated at 150° (10 min.). This when refluxed (18 hr.) with NaOEt–EtOH gives 1 : 4-diketo-3-(4′-nitrophenyl)tetrahydrophthalazine (XVII) [*Ag* salt (XVIII)], also obtained by $KMnO_4$ oxidation of 1-hydroxy-3-(4′-nitrophenyl)-3 : 4-dihydrophthalazine-4-acetic acid, and converted by boiling $Ac_2O$ into 4-*keto*-1-*acetoxy*-3-(4′-*nitrophenyl*)-3 : 4-*dihydrophthalazine*, m.p. 222°, also obtained from (XVIII) and $Ac_2O$, and hydrolysed by boiling EtOH–$H_2O$–HCl to (XVII). (XVIII) when refluxed with MeI–MeOH gives 4-keto-1-methoxy-3-(4′-nitrophenyl)-3 : 4-dihydrophthalazine. The following compounds are described: o-*carboxybenzo*-3′-*nitro*-, m.p. 193—194° with ring closure, resolidifying, and remelting at 217—219°, -2′-*nitro*-, m.p. 290—294°, -4′-*nitro*-2′-*methyl*-, m.p. 219°, -2′-*chloro*-4′-*nitro*-, m.p. 270—275°, -2′-*bromo*-4′-*nitro*-, m.p. 232° with ring closure, resolidifying and melting again at 280—282°, -2′ : 6′-*dichloro*-4′-*nitro*-, m.p. 192°, -2′ : 6′-*dibromo*-4′-*nitro*-, m.p. 200°, with ring closure, resolidifying and melting again at 227°, -*phenylhydrazide*; *phthalyl*-3′-*nitro*-, m.p. 227—228°, -2′-*nitro*-, m.p. 293—294°, -4′-*nitro*-2′-*methyl*-, m.p. 228°, -2′-*chloro*-4-*nitro*-, m.p. 267°, -2′-*bromo*-4′-*nitro*-, m.p. 282—283°, -2′ : 6′-*dichloro*-4′-*nitro*-, m.p. 202°, -2′ : 6′-*dibromo*-4′-*nitro*-, m.p. 230°, -*phenylhydrazide*; *Ag* salts of 1 : 4-diketo-3-(3′-nitrophenyl)- and -(4′-nitro-2′-methylphenyl)-tetrahydrophthalazine, also obtained from the appropriate substituted 3-phenylphthalaz-1-one; 1 : 4-*diketo*-3-(2′-*nitrophenyl*-, m.p. 293—294° (*Ag* salt), -2′-*chloro*-4′-*nitrophenyl*)-, m.p. 271—272° (*Ag* salt), -(2′-*bromo*-4′-*nitrophenyl*)-, m.p. 273—274°, -(2′ : 6′-*dichloro*-4′-*nitrophenyl*)-, m.p. 309—310°, -(2′ : 6′-*dibromo*-4′-*nitrophenyl*)-, m.p. 235—260°, -*tetrahydrophthalazine*; 4-*keto*-1-*methoxy*-3-(2′-*nitrophenyl*)-, m.p. 176—177°, -(2′-*chloro*-4′-*nitrophenyl*)-, m.p. 193—194°, -(2′-*bromo*-4′-*nitrophenyl*)-, m.p. 167—168°, -(2′ : 6′-*dichloro*-4′-*nitrophenyl*)-, m.p. 178—179°, -*phenyl*-, m.p. 109—111°, -3 : 4-*dihydrophthalazine*; 2 : 6-*dichloro*-, m.p. 133° (PhCHO *derivative*, m.p. 153°), and 2 : 6-*dibromo*-, m.p. 135—136° (two modifications; PhCHO *derivative*, m.p. 168—169°), -4-*nitrophenylhydrazine*. The Ag salt of 1 : 4-diketo-3-phenyltetrahydrophthalazine when refluxed with EtI and EtOH yields 4-keto-1-ethoxy-3-phenyl-3 : 4-dihydrophthalazine, an *O*-Et ether described previously as a *N*-Et ether (cf. A., 1887, 668; J.C.S., 1920, **117**, 719).

H. G. M.

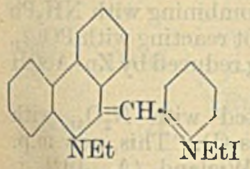
**Action of αγ-chlorobromopropane on 2-aminopyridine.** S. M. Scherlin and V. S. Velitschkin (J. Gen. Chem. Russ., 1935, **5**, 1586—1588).—2-Aminopyridine (I) and $CH_2Cl \cdot CH_2 \cdot CH_2Br$ (II) are allowed to interact at room temp., the reaction mixture is boiled for 20 hr., cooled, and the upper layer of unchanged (II) is removed. The lower layer is dissolved in aq. NaOH, and unchanged (I) is removed by steam-distillation. The *base* (III), b.p. 144—



(III.)

145°/10 mm., m.p. 55—56° (*picrate*, m.p. 172—173°; *hydrochloride*, m.p. 82—83°), is isolated from the residue. (III) is converted by Na in boiling EtOH into the corresponding $H_6$-derivative, b.p. 85—90°/10 mm. R. T.

**Cyanine dye series. V. Dyes derived from 9-methylphenanthridine.** L. G. S. Brooker and G. H. Keyes (J. Amer. Chem. Soc., 1936, **58**, 659—662; cf. this vol., 348).—The etho-*p*-toluenesulphonate (I) of 9-methylphenanthridine [*ethiodide* (II), m.p. 237—239° (decomp.), from (I) and aq. MeOH–KI] with 2-iodopyridine ethiodide in $Pr^aOH–NEt_3$ gives 27% of 1 : 1′-*diethyl*-3′ : 4′-*benzo-2-pyrido-2′-cyanine iodide* (III), m.p. 221—224° (decomp.). 1 : 1′-*Diethyl*-3 : 4-*benzo*-, m.p. 259—262° (decomp.), and 1 : 1′-*diethyl* - 3 : 4 : 5′ : 6′ - *dibenzo* - , m.p. 250—251° (decomp.), -2 : 2′-*cyanine iodides* are similarly prepared from 2-iodoquinoline ethiodide (IV) [with (II)] and 2-iodo-β-naphthquinoline ethiodide (V) [with (I)], respectively. (I) and $CH(OEt)_3$ in $C_5H_5N$, followed by KI, give 1 : 1′-*diethyl*-3 : 4 : 3′ : 4′-*dibenzo*-2 : 2′-*carbocyanine iodide*, m.p. 234—235° (decomp.). 1 : 1′-*Diethyl*-5′ : 6′-*benzo*-2-*pyrido*-2′-*cyanine iodide*, m.p. 268—270° (decomp.), is formed from 2-methylpyridine ethiodide, (V), and 1-methylpiperidine in EtOH. Improved preps. of 1 : 1′-diethyl-5 : 6-benzo- [from (IV) and β-naphthquinaldine etho-*p*-toluenesulphonate] (cf. Hamer, A., 1928, 307) and 1 : 1′-diethyl-5 : 6 : 5′ : 6′-dibenzo-2 : 2′ cyanine iodides (cf. Hamer and Kelly, A., 1931, 741) are given. The dyes containing the phenanthridine nucleus have no sensitising action; the absorption max. lie nearer the blue than those of the isomerides containing the β-naphthquinoline nucleus. H. B.



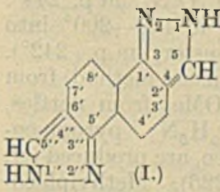
(III.)

**Orthochromatic sensitisation of photographic silver halide emulsions.**—See B., 1936, 477.

**Action of mixed organomagnesium derivatives on acetophenone semicarbazone.** (Mlle.) D. Biquard (Bull. Soc. chim., 1935, [v], **3**, 656—665).—Addition of acetophenonesemicarbazone (I) to MgEtBr or MgBuCl in anhyd. $Et_2O$ establishes the presence of 3 and 4 active H in cold and hot solution, respectively, and affords small amounts of unchanged (I), a little COPhMe, and 60—70% yields of a *substance* (II), $NH{<}\begin{matrix}CH{:}CPh\\CH{=}N\end{matrix}{>}NH$, m.p. 126° (*dibromide*, m.p. 145—148°; very hygroscopic *hydrochloride*; *platinichloride*, decomp. 252°). (II) is transformed by hot $Ac_2O$ into the $Ac_2$ derivative, m.p. 156° (*dibromide*, m.p. 170°), hydrolysed by HCl to (II) and by KOH to the $Ac_1$ compound, m.p. 235°. Treatment of the product from (I) and MgEtBr with AcCl or $Ac_2O$ (=MgEtBr) in $C_6H_6$ gives two *compounds*, $N{<}\begin{matrix}CH{=}CPh\\CAc{\cdot}NAc\end{matrix}{>}NH$, m.p. 273°, and $N{<}\begin{matrix}CH_2{\cdot}CPh\\CAc{\cdot}NAc\end{matrix}{>}N$, m.p. 203°, readily separable from one another owing to their differing solubility in HCl. The constitutions assigned are supported by the spectroscopic evidence. H. W.

**Manufacture of *iso*alloxazine compounds.**—See B., 1936, 363.

**3 : 4 : 3″ : 4″-Dipyrazolo-1′ : 2′ : 5′ : 6′-naphthalene.** V. Veselý and A. Medvedeva (Coll. Czech. Chem. Comm., 1936, **8**, 125—129).—2 : 6-$C_{10}H_6Me_2$ is converted by $HNO_3$ (*d* 1·51)–AcOH at 100° into its 1 : 5-$(NO_2)_2$-derivative, m.p. 179° [Mayer *et al.*, A., 1922, i, 999; the $(NO_2)_2$-derivative, m.p. 186°, is probably the 1 : 8-compound], reduced by Fe–aq. AcOH–$COMe_2$ to the $(NH_2)_2$-derivative, the $Ac_2$ derivative of which is converted by $N_2O_3$–AcOH at 40—50° into crude 1 : 5-*di*(*nitrosoacetamido*)-2 : 6-*dimethylnaphthalene*, m.p. 116—126° (decomp.), converted by boiling $C_6H_6$ into 3 : 4 : 3″ : 4″-*dipyrazolo*-1′ : 2′ : 5′ : 6′-*naphthalene* (I) (1 : 1″-$Ac_2$ derivative, m.p. >330°). J. W. B.



(I.)

**Leaf xanthophylls.** H. H. Strain (Science, 1936, **83**, 241—242).—When leaf xanthophyll, freed from leaf constituents, is adsorbed on Tswett columns, three or four pigments resembling cryptoxanthin rapidly pass through the column. They are followed on the column by lutein (I) and iso*lutein* (II), which is optically inactive and gives in $Et_2O$ a deep blue colour with conc. HCl. Zeaxanthin (III), present in small amount, is found on the column above (II); it occurs in the leaves of barley, carrots, filaree, lettuce, sunflower, squash, and spinach. (III) is followed on the column by a *pigment* ($[\alpha]^{18}_{6678}$ +75°, in $CHCl_3$) having absorption curves similar to those of flavoxanthin. Another similar *pigment* having the same absorption curve, but with $[\alpha]^{18}_{6678}$ −56° in $CHCl_3$, is adsorbed next on the column, and is followed by considerable amounts of a xanthophyll the absorption curves of which are intermediate in shape between those of (I) and the flavoxanthin-like pigments. Several xanthophylls occurring in small amounts are adsorbed finally. L. S. T.

**Chlorophyll. LXVI. Comparative oxidation of chlorophyllide and derivatives.** H. Fischer and S. Breitner. **LXVII. Active hydrogens in chlorophyll derivatives. V.** H. Fischer and S. Goebel (Annalen, 1936, **522**, 151—167, 168—185).—LXVI. Methylethylmaleimide (I) (accompanied, in some cases, by hæmatic acid) is formed in varying yield by oxidation ($CrO_3$, cold aq. $H_2SO_4$) of methylchlorophyllide *a*, phæophorbide *a**, dihydrophæophorbide *a*, chlorins $e_4$*, $e_6$*, and $p_6$*, dihydrochlorins $e_4$, $e_6$, and $p_6$, rhodochlorin, phæopurpurins 7* and 18*, dihydrophæopurpurins 7 and 18, ψ-chlorin $p_6$, rhodo-, verdo-, and ψ-verdo-porphyrins, and mesoporphyrin and its Cu salt. The yield is < that from derivatives from blood pigment. Certain irregularities are noted. Compounds marked *, which contain the $C_2{\cdot}CH{:}CH_2$ group, generally give about 50% of the amount of (I) obtained from their dihydro-derivatives. In accordance with expectation, (I) is not formed from unreduced derivatives of chlorophyll *b*, *i.e.*, compounds containing $C_2{\cdot}CH{:}CH_2$ and $C_3{\cdot}CHO$; rhodin $g_7$ and neorhodinporphyrin $g_3$ (II) give citraconimide (arising from ring III of the chlorophyll mol.). Dihydrorhodin $g_7$, dihydrophæophorbide *b*, and rhodinporphyrin $g_8$ (III) afford (I), since they contain the $C_2{\cdot}Et$ group.

The *Cu* salt, m.p. 237°, of rhodin *g* $Me_3$ ester is reduced catalytically in $COMe_2$ or AcOH to the Cu salt, [α] −366°, of dihydrorhodin *g* $Me_3$ ester. The *Cu* salt of rhodinporphyrin $g_7$ has m.p. 264°. The oxime of (II) (as ester) is dehydrated ($Ac_2O$–KOAc) to the corresponding *nitrile*, $C_{33}H_{33}O_2N_5$, m.p. 244°. (III) is converted by 20% HCl at 190—200° into 3-demethylphylloporphyrin (*Me* ester, m.p. 242°). Phæophorbides *a* and *b*, obtained (usual method) from chlorophyll extracted by 90% $COMe_2$ from nettles, lose $CO_2Me$ when heated in $C_5H_5N$; pyrophæophorbin *a* and *b*, which are OMe-free, are produced (cf. Conant and Hyde, A., 1930, 225). Methylphæophorbide *a* and *b* similarly lose $CO_2Me$ and give pyrophæophorbide *a* and *b*, respectively. These results are considered to support the view (cf. Stoll, this vol., 392) that the original phytyl group is attached to $\cdot CH_2\cdot CH_2\cdot CO_2H$. Chlorophyll *a* (but no *b*) is present in the algæ *Asacusa nori*, *Bangia fuscopurpurea*, and *Polysiphonia nigrescans*.

[With K. HERRLE.] Phyllochlorin Me ester is reduced ($H_2$, Pd, $COMe_2$) to *dihydrophyllochlorin Me* ester, m.p. 148°, $[\alpha]^{20}_{690-700}$ −619° in $COMe_2$, which is identical (spectrum; Cu salt; alkaline degradation to phylloporphyrin) with the synthetic phyllochlorin of Treibs and Wiedemann (A., 1928, 1383).

LXVII. The no. of active H present in about 70 compounds (derivatives of phæophorbides *a* and *b*; phæoporphyrins *a* and *b*; phylloerythrins; chlorins; chloroporphyrins; rhodins; rhodinporphyrins; purpurins; phylloporphyrins) are determined by Schmitz-Dumont's method (A., 1934, 313). In most cases the results are in agreement with structures previously proposed. The vals. for verdo- and ψ-verdo-porphyrin esters are, however, inexplicable. The following conclusions are reached. The phæophorbides contain 2NH and an enolic OH (formation of which is suppressed by oximation); the $C_{10}\cdot CO_2Me$ exerts a strong labilising action on the $C_{10}\cdot H$. Chlorins and rhodins are analogously constituted, the latter having $C_3\cdot CHO$ for $C_3\cdot Me$; these results are not in agreement with those deduced by Conant *et al.* (A., 1934, 1371) from potentiometric titrations. The relationship between green and red compounds in the porphyrin and purpurin series is discussed. Absorption spectra of many of the phyllins (prepared during the above determinations) and some of the original compounds are given. H. B.

**Porphyrin synthesis. Synthesis of porphin.** P. ROTHEMUND (J. Amer. Chem. Soc., 1936, **58**, 625—627; cf. A., 1935, 1510).—Pyrrole (I) and $CH_2O$ in MeOH–$C_5H_5N$ at 90—95° (sealed tube) give porphin (II) (*phyllin*; *hæmin*; complex *Cu* salt); at 145—155°, a porphyrin of lower HCl val., which differs spectroscopically from (II), is formed. Absorption spectra for (II) and its salts are given. αβγδ-Tetra-methyl-, -ethyl-, -propyl-, -phenyl-, and -furyl-porphins (not described) are similarly obtained from (I) and MeCHO, EtCHO, PrCHO, PhCHO, and furfuraldehyde, respectively. Porphyrin formation also occurs (shown spectroscopically) with $CCl_3\cdot CH(OH)_2$, $CHO\cdot CO_2H$, $o$-$NO_2\cdot C_6H_4\cdot CHO$, vanillin, $p$-$NMe_2\cdot C_6H_4\cdot CHO$, and pyrrole-2-aldehyde. H. B.

**Optical absorption of porphyrins.**—See this vol., 662.

**Preparation of 1-methyl-α-naphthoxazole.** J. FRASER and F. M. HAMER (J.S.C.I., 1936, **55**, 119—120T).—The original method (A., 1934, 115) has been improved to give a 39% yield.

**Dioximes. CIX, CX.** G. PONZIO (Gazzetta, 1936, **66**, 114—119, 119—126).—CIX. The action of bases on α-phenylglyoxime peroxide (I) (3-phenyl-1 : 2 : 5-oxadiazole 5-oxide) gives a product which was regarded by Wieland and Semper (A., 1908, i, 108) as a hydroxyphenylfurazan (4-hydroxy-3-phenyl-1 : 2 : 5-oxadiazole), but is now shown to be α-oximinophenylacetonitrile oxide (II). (I) resembles (II) in behaviour towards AcOH, $EtCO_2H$, $NH_3$, $NH_2Ph$, etc., MgMeI, $Ac_2O$, $Bz_2O$, aq. EtOH, and boiling 20% HCl, but differs from it in not combining with $NH_2Ph$ in non-hydroxylic solvents, in not reacting with $POCl_3$, in not polymerising, and in being reduced by Zn–AcOH to α-phenylglyoxime.

CX. α-Phenylglyoxime treated with $N_2O_4$, with hot MeOH, and with HCl, gives (I). This, new m.p. 111—112°, was regarded by Wieland (A., 1921, i, 606) as an unstable form from which crystallisation from $C_6H_6$, EtOH, etc. gave a stable product. (I) exists, however, in one form only, and the recryst. product, m.p. 85—95°, is a mixture of (I) and (II), as is shown by its giving chlorophenylglyoxime when treated with HCl, and by the formation of oximinophenylacetonitrile on reduction. Pure (I) suspended in EtOH and treated with $NH_2Ph$ yields OH·N:CPh·C(:NPh)·NH·OH. In 50% EtOH, *(I)* gives a product which with $Cu(OAc)_2$ gives a ppt. *from* which $H_2SO_4$ liberates 4-benzamido-3-phenyl-1 : 2 : 5-oxadiazole, with phenylmetazonic acid. With xylene at 137—138° (I) gives β-phenylglyoxime peroxide; with AcOH, 5-hydroxy-3-phenyl-1 : 2 : 4-oxadiazole (the sole product when $EtCO_2H$ is used) and hydroxyphenylglyoxime. (I) is reduced by $SnCl_2$ to 3-phenyl-1 : 2 : 5-oxadiazole. With MgMeI, the *compound*, OMgI·N:CPh·CMe:N·OMgI is formed, hydrolysed by HCl to PhCN and α-phenylglyoxime; α-diphenylglyoxime is obtained by using MgPhBr. With $Bz_2O$ (I) gives the $Bz_3$ derivative, m.p. 165—166° (decomp.), of hydroxyphenylglyoxime, hydrolysed by EtOH to the $Bz_2$ derivative, and by NaOH to 5-hydroxy-3-phenyl-1 : 2 : 5-oxadiazole. E. W. W.

**Action of acetic anhydride on dibenzylidenehydrazine.** J. B. EKELEY and J. W. LEFFORGE (J. Amer. Chem. Soc., 1936, **58**, 562—563).—$(\cdot N:CHPh)_2$ (1 mol.) and $Ac_2O$ (about 3 mols.) at 127°/624 mm. give $(\cdot NHAc)_2$ (19%), 2 : 5-dimethyl-1 : 3 : 4-oxadiazole (14%), b.p. 165—169°/624 mm. [formed by dehydration of $(\cdot NHAc)_2$], and NHAc·N:CHPh (40%). Addition of $Ac_2O$ to ·N:CHAr thus gives ·NAc·CHAr·OAc (cf. A., 1932, 384). H. B.

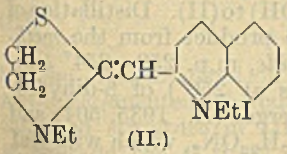
**1-Methylbenzthiazole.** J. FRASER and F. M. HAMER (J.C.S., 1936, 507).—1-Methylbenzthiazole has m.p. 14°. F. R. S.

**Reactivity of the imino-group in 1-imino-2-methylbenzthiazoline.** L. M. CLARK (J.C.S., 1936, 507).—1-Imino-2-methylbenzthiazoline with $NH_2Ph$ gives 1-*anilo-*, m.p. 95·5°, and with phenylthiocarbamide forms 1-*phenylthiocarbamylimino-2-methylbenzthiazoline*, m.p. 184°, and a substance, m.p. 261°;

with quinaldine, it yields 2-*methylthio-ψ-cyanine*, m.p. 165° *platinichloride*). F. R. S.

**Chemical nature of vitamin-$B_1$.**—See this vol., 646.

**Cyanine dye series. VI. Dyes derived from 2-methylthiazoline.** L. G. S. Brooker (J. Amer. Chem. Soc., 1936, **58**, 662—665; cf. this vol., 349).—2-*Methylthiazoline ethiodide* (I), m.p. 190—193° [the *methiodide* has m.p. 241—242° (decomp.)], and 2-iodoquinoline ethiodide in EtOH–$NEt_3$ give 3 : 1′-*diethylthiazolino-2′-cyanine iodide* (II), m.p. 226—227°. 2-Iodopyridine ($Pr^aOH$–$NEt_3$), 2-iodo-β-naphthquinoline (EtOH–$NEt_3$), and quinoline (EtOH–KOH) ethiodides with (I) afford 3 : 1′-*diethylthiazolino-2′-pyridocyanine*, m.p. 203—206°, 3 : 1′-*diethyl-5′ : 6′-benzthiazolino-2′-cyanine*, m.p. 263—266°, and 3 : 1′-*diethylthiazolino-4′-cyanine*, m.p. 223—224°, *iodides*, respectively. 2-Methylthiazoline metho-*p*-toluenesulphonate and $CH(OEt)_3$ in $C_5H_5N$, followed by KI, give 3 : 3′-*dimethylthiazolinocarbocyanine iodide*, m.p. 250—252° [7-*Et* derivative, m.p. 248—250°, obtained using $CEt(OMe)_3$], whilst (I) and $CH(OEt)_3$ similarly afford 3 : 3′-*diethylthiazolinocarbocyanine iodide*, m.p. 256—258° [7-*Et* derivative, m.p. 182—184°, formed from 2-methylthiazoline etho-*p*-toluenesulphonate and $CEt(OMe)_3$ followed by KI]. 2-p-*Dimethylaminostyrylthiazoline ethiodide*, m.p. 219—220°, is obtained from (I) and $p$-$NMe_2$·$C_6H_4$·CHO in MeOH–piperidine. The new dyes are sensitisers; they absorb at shorter λλ than analogous compounds prepared from other heterocyclic bases. H. B.



(II.)

***d*-Nornicotine.** C. S. Hicks (Austral. J. Exp. Biol., 1936, **14**, 39—43).—*d*-Nornicotine when methylated gives nicotine methiodide and when dehydrogenated (Pt-asbestos 320—330°) yields 2-(3-pyridyl)-pyrrole. W. McC.

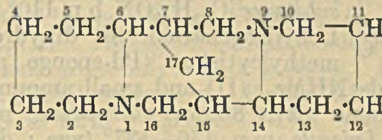
**Tobacco bases. VI. Synthesis of myosmine.** E. Späth and L. Mamoli (Ber., 1936, **69**, [*B*], 757—760; cf. this vol., 489).—Pyrrolidone and $Bz_2O$ at 180° give 1-benzoylpyrrolidone, m.p. 92—93°, which, condensed with Et nicotinate (NaOEt), gives 1-benzoyl-3-nicotinoylpyrrolid-2-one. This (without isolation) is treated with fuming HCl whereby debenzoylation, decarboxylation, ring fission and subsequent closure lead in one operation to myosmine (2-3′-pyridyl-4 : 5-dihydropyrrole).

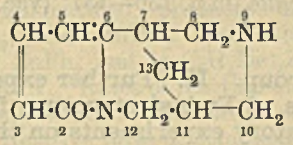
Reply is made to Reynolds and Robinson (this vol., 486). H. W.

**Lupin. IX. Monolupine, a new alkaloid from *Lupinus caudatus*, Kellogg.** J. F. Couch (J. Amer. Chem. Soc., 1936, **58**, 686—687).—*Monolupine* (I), $C_{16}H_{22}ON_2$ (+0·5$H_2O$), b.p. 257—258°/4 mm., $[\alpha]_D^{29}$ −40·81° in EtOH [*dihydrochloride* (+2$H_2O$), m.p. 115—116° (rapid heating), which when dried at 110° gives the *hydrochloride*, m.p. 280°; *aurichloride* (+3$H_2O$), m.p. 167—168° (decomp.); *methiodide* (+$H_2O$), m.p. 257°], is isolated (method : A., 1935, 97) in 0·44—0·5% yield from the dry plant. (I) resembles anagyrine, is unsaturated ($KMnO_4$), but could not be reduced (Adams; electrolytic). *L. caudatus* thus differs from *L. palmeri* (*loc. cit.*). H. B.

**Numbering of sparteine molecule and its derivatives.** J. F. Couch (J. Amer. Chem. Soc., 1936, **58**, 688).—Structure (I) for sparteine shows its symmetrical character and relationship to other lupin alkaloids and to cytisine (II). Lupanine, hydroxylupanine, and anagyrine become 2-keto-, 10-hydroxy-2-keto-, and 2-keto-3 : 4 : 5 : 6-tetradehydro-sparteine, respectively. Possible modes of biosynthesis of (I) and (II) are indicated.

(I.)





(II.)

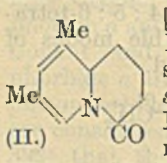
H. B.

**Gramine.** H. von Euler, H. Erdtman, and H. Hellström (Ber., 1936, **69**, [*B*], 743—747).—Although spectroscopically similar, gramine (I) is not identical with 2-dimethylaminomethyl- or 3-dimethylamino-2-methyl-indole. Distillation of (I) with Zn dust affords skatole in too small amount to indicate its constitution. (I) gives a red pine-shaving reaction but not the Ehrlich reaction. It gives a faint red colour with $p$-$SO_3H$·$C_6H_4$·$N_2Cl$ in alkaline solution. It appears to be hydrolysed by acids to a substance not identical with atroxindole. It does not afford AcOH when oxidised by $CrO_3$. A completely satisfactory structure cannot at present be assigned to (I), which is regarded provisionally as 2-methylethylaminoindole. H. W.

**Cactus alkaloids. XVII. Optical activity of pellotine.** E. Späth and F. Kesztler (Ber., 1936, **69**, [*B*], 755—757).—Attempts to resolve *dl*-pellotine into its optical antipodes by *d*-tartaric acid in MeOH under unusually cautious conditions lead to the isolation of l-*pellotine* (I), $[\alpha]_D^{17}$ −15·2° in $CHCl_3$, for which optical homogeneity is not claimed. (I) is slowly racemised in $H_2O$ at 15—20°, very rapidly in alkaline solution, less readily in the presence of acid. Distillation in high vac. causes complete inactivation. Since the alkaloid is very readily racemised and the accompanying alkaloids are optically active it is concluded that the plants form the active modification which becomes racemised probably within the living cell, at any rate during storage and extraction. H. W.

**Action of perbenzoic acid on cinchona-bark alkaloids.** J. Becker and J. Suszko (Arch. Chem. Farm., 1934, **1**, 199—205).—Oxidation takes place at the quinuclidine N, the same amino-oxides being formed as with $H_2O_2$. Advantages of the use of $BzO_2H$ are discussed. Ch. Abs. (*r*)

**Dehydrogenation of cytisine and product of the degradation of this base.** E. Späth and F. Galinovsky (Ber., 1936, **69**, [*B*], 761—766).—Dehydrogenation of cytisine with Pd-sponge at 270—280° gives 2-hydroxy-6-methylquinoline with much resinous material. Similar treatment of tetrahydro- and octahydro-hemicytisylene affords 3 : 5-*dimethyl*-2-*propylpyridine* (I), b.p. (bath) 100—110°/10 mm. (*picrate*, m.p. 150—151°; *methiodide*, m.p. 127—128°), oxidised by acid $KMnO_4$ to 3 : 5-dimethylpyridine-2-carboxylic acid and 5-methylnicotinic acid, and 8-*keto*-2 : 4-*dimethyl*-ψ-*quinolizine* (II), m.p. 83° [*hemihydrate*, m.p. 64—65°; *picrate*, m.p. 149—150° (vac.; decomp.)], which absorbs $4H_2$ (Pd–C in AcOH) giving the *substance*, $C_{11}H_{19}ON$, b.p. 110°/0·01 mm. Dehydrogenation of dihydrode-*N*-dimethylcytisine (Pd-sponge at 230—270°) yields $NHMe_2$, (II) and small amounts of (I). α-Norlupinone gives 8-*keto*-ψ-*quinolizine*, m.p. 72—73° (vac.) [*picrate*, m.p. 136—137° (vac.; decomp.)], and conyrine. H. W.



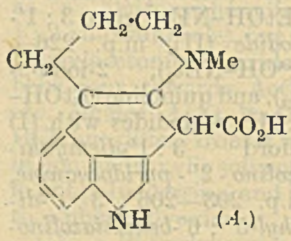
(II.)

**Cytisine group. II. Further experiments on the synthesis of Ewins' structure for cytisine. III. Exploratory experiments on the synthesis of cytisine, sparteine, lupinine, and allied alkaloids.** S. N. Chakravarti and P. L. N. Rao (J. Annamalai Univ., 1936, 5, 254—258, 259—268).—II. Further unsuccessful attempts (cf. A., 1934, 195) are described. 6-Nitro-3-methylcinnamic acid (*loc. cit.*) has been reduced ($FeSO_4$–$NH_3$) to the 6-$NH_2$-compound, m.p. 195°, and the *hydrochloride* of this diazotised and reduced ($Na_2SO_3$–HCl–Zn) to 1-*amino*-6-*methyldihydrocarbostyril*, m.p. 117° (with some 6-*methyldihydrocarbostyril*, m.p. 132—133°), in amount insufficient for cyclisation through 8-$CH_2$. Attempted oxidation of 6 : 8-dimethylquinoline to 6-methylquinoline-8-carboxylic acid by $CrO_3$, $SeO_2$, or dil. $HNO_3$ gives unsatisfactory results; with a large excess of $CrO_3$, *quinoline*-6 : 8-*dicarboxylic acid*, m.p. > 300° is formed. The 6 : 8-$Me_2$ compound is converted by Br–HBr in $CHCl_3$ into the *hydrobromide*, m.p. 125—140° (decomp.), of the $Br_2$-compound, which loses HBr at 160°, and when heated in $CHCl_3$ gave, in an experiment which could not be repeated, a *bromodimethylquinoline*, m.p. 58°.

III. The successful prep. of 2-chloropyridine (I) from 1-methylpyridone (J.C.S., 1915, 107, 690) is confirmed (cf. A., 1932, 66). Attempts to condense (I) with $CH_2(CO_2Et)_2$ or with $CH_2[CH(CO_2Et)_2]_2$ were unsuccessful. The last is converted into $CH_2[CH(CO{\cdot}NH_2)_2]_2$, which at 250° gives a poor yield of $CH_2(CH_2{\cdot}CO{\cdot}NH_2)_2$, reduced to a basic substance. Theoretical schemes for synthesising lupinine, sparteine, and cytisine are outlined. E. W. W.

**Ergot alkaloids. VIII. Synthesis of 4-carbolinecarboxylic acids. IX. Structure of lysergic acid.** W. A. Jacobs and L. C. Craig (J. Biol. Chem., 1936, 113, 759—765, 767—778).—VIII. Largely a more detailed account of work previously reviewed (this vol., 216). 3 : 4-*Dimethyl*-3 : 4 : 5 : 6-*tetrahydro*-4-*carboline*-5-*carboxylic acid*, m.p. 248° (decomp.) (previous darkening and softening), and the non-cryst. product formed from *N*-methyltryptophan, 10% MeCHO, and *N*-$H_2SO_4$, are both oxidised ($K_2Cr_2O_7$, dil. AcOH) with loss of $CO_2$ to 4-*methyl*-4-*carboline* (N-*methylharman*), m.p. 180° (previous darkening) [*sulphate*, m.p. 273° (decomp.); *dichromate*]. 3-Methyltetrahydro-4-carboline-5-carboxylic acid (*loc. cit.*) similarly gives harman, whilst lysergic (I) and dihydrolysergic (II) acids afford amorphous acidic material.

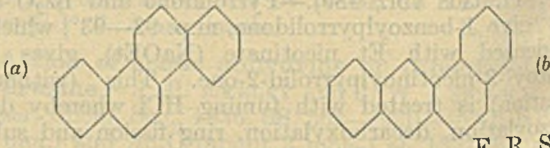
IX. The structure previously suggested (this vol., 488) for (I) is revised to (*A*). Reduction ($H_2$, $PtO_2$, AcOH) of the alkaloid, $C_{19}H_{23}O_2N_3$ (ergometrine, etc.; cf. Kharasch *et al.*, this vol., 489), gives a $H_2$-*derivative*, m.p. 225—230° (decomp.) (sinters at 110°), hydrolysed (14% MeOH-KOH) to (II). Distillation of the product from the *methiodide*, m.p. 253—254° (sinters at 250°) of β-dihydrolysergol (A., 1935, 504) and $Ag_2O$ affords an oily *base*, $C_{17}H_{22}ON_2$, which with MeI followed by $Ag_2O$ gives $NMe_3$ [in accordance with structure (*A*)] and resin. The remainder of the paper has been abstracted previously (*loc. cit.*). H. B.



(*A*.)

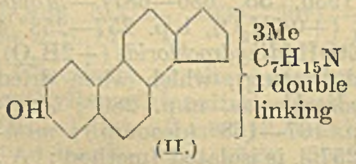
**Optical properties of ergometrine.** I. Bennekou and S. A. Schou (Dansk Tidsskr. Farm., 1936, 10, 105—108).—The blue fluorescence of ergometrine (I) solutions under ultra-violet radiation persists after its removal. The absorption max. of the spectrum of (I) solutions changes from 3160 to 2890 A, whilst the other ergot alkaloids show a gradual decrease of absorption, owing to decomp. M. H. M. A.

**Veratrine alkaloids. III. Preparation of cevanthrol, and *X*-ray crystallographic examination of cevanthrol and cevanthridine.** B. K. Blount and (Miss) D. Crowfoot (J.C.S., 1936, 414—415).—Se dehydrogenation of cevine gives a base, cevanthridine (I) (cf. A., 1935, 505), and a phenolic compound, *cevanthrol* (II), $C_{17}H_{16}O$, m.p. 197—198° (*Ac* derivative, m.p. 138—139°). The results of *X*-ray crystallographic examination of (I) and (II) support a phenanthrene ring structure for (II) and a ring system of type (*a*) or (*b*) for (I).


(*a*) (*b*)

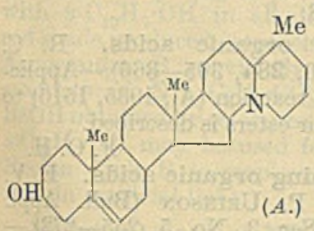
F. R. S.

**Solanine and solanidine.** A. Soltys and K. Wallenfels (Ber., 1936, 69, [*B*], 811—818).—Repeated extraction of solaneine (I) with $COMe_2$ and $Et_2O$ causes its complete separation into solanidine (II) and solanine (III). (I) should therefore be deleted from the lit. Hydrolysis of (III) gives about 37·5% of (II) and 12·5% of solanthrene (IV). It is therefore very improbable that (IV) is formed from its proper glucoside. (II) does not yield (IV) when hydrolysed. The presence of one and two double linkings in (II) and (IV), respectively, is con-



(II.)

firmed, the double linkings in (IV) being hydrogenated with equal facility. To avoid confusion it is recommended that the completely saturated tetrahydrosolanthrene be designated solanidane. (II) is therefore solanidenol and its derivatives are termed in accordance with the Geneva nomenclature except that the name solanidine is retained. (II) affords a *mono-ozonide* which does not permit degradation of the mol., since (II) is regenerated under varied conditions of fission. With digitonin (II) gives a ppt. suggesting a constitutional relationship with the sterols; this is confirmed by the dehydrogenation of solanidiene by Se to methyl*cyclo*pentenophenanthrene. The present established structure of (II) is as shown. Attempts to degrade the $C_7H_{15}N$ residue were unsuccessful. *Solanine methiodide*, m.p. 230°, when treated with moist $Ag_2O$ and then distilled yields (II). Since N is *tert.* and the group $C_7H_{15}N$ is unusually stable the structure (*A*) is suggested for (II). H. W.



(*A*.)

**Deltaline, a new alkaloid from *Delphinium occidentale*, S. Wats.** J. F. Couch (J. Amer. Chem. Soc., 1936, 58, 684—685).—Details are given for the isolation of *deltaline* (I), $C_{19}H_{24}ON(OH)_3(OMe)_2$, m.p. 180—181°, $[\alpha]_D^{24}$ −27·86° in EtOH [$Ac_3$ derivative, amorphous, m.p. 270—272°; *aurichloride* ($+3H_2O$), m.p. 120—125°], from the dry plant, which contains 0·98% of total alkaloids [mainly (I)]. (I) is isomeric but not identical with delcosine (Markwood, A., 1925, i, 762). H. B.

**Chemistry and pharmacological action of *Toddalea aculeata*.** B. B. Dey, P. P. Pillay, J. C. David, and N. Rajamanikam (Indian J. Med. Res., 1935, 22, 765—770).—Two alkaloids, *toddaline* (I), $C_{20}H_{21}O_4N$, m.p. 269—270° (*hydrochloride*, m.p. 205—206°; several other *salts* described), and *toddalinine*, a N-free lactone, and a glucoside have been isolated from *Toddalea* root-bark. Both alkaloids give marked colour reactions. Crude (I) is converted by rubbing with EtOH–$NH_3$ into an insol. cryst. powder, m.p. 204—206°, which gives the same hydrochloride, and is probably another form of (I). The pharmacological action of (I) is described. R. N. C.

**Toxic principle of ragwort (*Senecio Jacobæa*, L.) I.**—See this vol., 652.

**Bark of *Moringa pteryosperma*.**—See this vol., 768.

**2-Chloro-6-nitrobenzaldimercurioxide.**—See B., 1936, 361.

**Constitution of mixed organo-magnesium compounds.** C. Duval (Compt. rend., 1936, **202**, 1184—1186).—When MgPhBr (I) in $Et_2O$ in an atm. of $N_2$ at 0° is electrolysed (cf. A., 1935, 1088), only Mg goes to the cathode. The anodic fluid contains Mg, Br (Mg/Br=1/2), $C_6H_6$, and $Et_2O$. If 8-hydroxyquinoline is introduced into the cell, the yellow colour due to $Mg^{II}$ is seen at the cathode, and at the anode only after hydrolysis, which indicates that part of the Mg in (I) is non-ionisable. The formula of (I) is probably $[MgPh_2Br_2(Et_2O)_2]Mg$ (cf. A., 1912, i, 753). J. L. D.

**Relative reactivities of organometallic compounds. VIII. Aluminium and zinc.** H. Gilman and K. E. Marple (Rec. trav. chim., 1936, 55, 133—144).—$AlPh_3$ (I) and $(p\text{-}C_6H_4Me)_3Al$ (II), best prepared from $HgR_2$ and Al in xylene, under $N_2$, and *Al tri*-n-*propyl*, b.p. 137—138°/22 mm., obtained from $MgPr^aBr$ and $AlCl_3$ in $Et_2O$, combine with PhNCO to form NHPhBz, $p\text{-}C_6H_4Me\cdot CO\cdot NHPh$, and $COPr^a\cdot NHPh$; with $CO_2$, (II) gives $p\text{-}C_6H_4Me\cdot CO_2H$, and with $COPh_2$, $p\text{-}C_6H_4Me\cdot CPh_2\cdot OH$; (I) similarly yields $CPh_3\cdot OH$. Passage of $O_2$ into a solution of (II) in cold xylene gives only 8% of *p*-cresol. (II) combines with PhCHO to form $p\text{-}C_6H_4Me\cdot CHPh\cdot OH$, and with PhCN to form $p\text{-}C_6H_4Me\cdot COPh$. With EtOBz or PhOBz, unidentified products are obtained. $ZnPh_2$, $ZnEt_2$, and $ZnPr^a{}_2$ react similarly with PhNCO; and $ZnPh_2$ and $(p\text{-}C_6H_4Me)_2Zn$ with $CO_2$, $COPh_2$, and PhCN. Rates of reaction of the above Al and Zn compounds are slower than those of Grignard compounds. Relative rates of combination of $AlPh_3$, $BPh_3$, $ZnPh_2$, $AlPr^a{}_3$, $BPr^a{}_3$, $ZnPr^a{}_2$, $(p\text{-}C_6H_4Me)_3Al$, and $(p\text{-}C_6H_4Me)_2Zn$ with Michler's ketone are tabulated, and the colour reaction with the latter is examined and used as a means of studying rates of reaction with PhCHO, $COPh_2$, and PhCN. The decreasing orders of reactivity $\cdot CHO > \cdot COPh > \cdot CN$, and $AlR_3 > BR_3 > ZnR_2$, are observed. Al displaces Hg more rapidly from $HgR_2$ compounds (R=aryl) than does Zn. The low reactivity of $AlR_3$ compounds makes it improbable that these are intermediates in the Friedel–Crafts reaction. E. W. W.

**Acridine salts of adenosinepolyphosphoric acids.** T. Wagner-Jauregg (Z. physiol. Chem., 1936, **239**, 188—194).—The acids yield cryst. $H_2O$-sol. (hot) *salts* with acridine (I) as follows: adenosine-tri- (II)+2(I), m.p. 209°, di- (III)+(I), m.p. 215°, -mono-phosphoric acid +(I), m.p. 208°, and also $2H_4P_2O_7+3(I)$, m.p. 258—260°. The salt of (III) is least sol. in hot $H_2O$. (II) also yields a salt with 3(I). $NaNO_2$ in 55% AcOH converts (II) into inosinetriphosphoric acid (cf. Lohmann, A., 1931, 1184) and not into an isomeride of (II) (cf. Barrenscheen *et al.*, A., 1933, 1202). W. McC.

**Structure of yeast nucleic acid.** K. Hagenguth (Z. physiol. Chem., 1936, **239**, 127—134).—Small yields of cytosylic (*$Hg^{II}$*, *$UO_2$*, *Pb*, and *brucine*, m.p. 189—190°, salts) and uracylic acid (*Pb* salt) are obtained from yeast nucleic acid by hot acid hydrolysis followed by pptn. with $Ag_2SO_4$, etc. W. McC.

**Isolation of a fourth crystallisable jack bean globulin by digestion of canavalin with trypsin.**—See this vol., 768.

**Determination of nitrogen in compounds containing halogens by the hydrogenation method.** H. ter Meulen and H. J. Ravenswaay (Chem. Weekblad, 1936, **33**, 248—249).—Satisfactory results are obtained with compounds of high halogen contents when a few g. of soda-lime are placed in front of the catalyst as well as behind it. S. C.

**Determination of nitrogen by Kjeldahl's method. Ammonia distillation.**—See this vol., 694.

**Determination of organic sulphur. I. Parr bomb method.** H. C. Chiang and C. L. Tseng (Sci. Rep. Nat. Univ. Peking, 1936, 1, 19—41).—S in $CS(NH_2)_2$, $SHBu^a$, and $p$-$C_6H_4Me{\cdot}SO_2Cl$ is determined by explosion with $Na_2O_2$ and lactose with or without $KClO_3$ or $KClO_4$ and subsequent gravimetric or volumetric determination of $SO_4''$. R. S. C.

**Principles and methods of a chemical morphology of carbon compounds.** C. Weygand (Angew. Chem., 1936, 49, 243—251).—The morphological study of cryst. org. compounds is suggested as an aid to identification, and suitable microscopic methods are described. M. S. B.

**Analysis of *S*-methyl compounds by demethylation with hydrogen iodide.** (Mlle.) A. Lacourt (Bull. Soc. chim. Belg., 1935, 44, 665—673).—Details are given for the semi-micro-determination of ·SMe by heating the compound with HI ($d$ 1·7); the resulting MeI vapours are freed from HI and $H_2S$ by means of $Na_2CO_3$–$Na_2S_2O_3$ and $CdSO_4$–$Na_2S_2O_3$ solutions and are determined in the usual way. SMe compounds are demethylated at a lower temp. than :NMe compounds, permitting the separate determination of these groups in compounds containing them both. H. G. M.

**Oxidimetric analysis of binary mixtures of organic compounds.** H. C. S. Snethlage (Rec. trav. chim., 1936, 55, 58—60).—The method described for pure substances (A., 1935, 1390) may be used for binary mixtures by using $K_2Cr_2O_7$ in 40% and 80% $H_2SO_4$, provided one of the components is not attacked and the other completely oxidises under the milder conditions. H. G. M.

**Titrimetric colorimetry.**—See this vol., 692.

**Diazometric method for the determination of diene hydrocarbons.** A. P. Terentiev, E. V. Vinogradova, and G. D. Galpern (Compt. rend. Acad. Sci. U.R.S.S., 1935, 4, 267—272).—Diazotised $p$-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ (I) reacts quantitatively with $\Delta^{1:3}$-dienes, but not at all with aromatic hydrocarbons or compounds with conjugated hetero-atoms (cf. lit.); one mol. of (I) reacts with one mol. of diene. Excess of (I) is used and the excess determined with β-$C_{10}H_7{\cdot}OH$. The method is suitable for the determination of dienes in mixtures of hydrocarbons of various types. H. G. M.

**Systematic detection of acetate.** L. J. Curtman and A. A. Polachek (Rec. trav. chim., 1936, 55, 153—156).—The green ppt. of $Cu_4O_3Cl_2$ obtained when a solution containing OAc′ is boiled with $CuCl_2$ (Reynoso, Compt. rend., 1855, 41, 278), when used as a qual. test (Field, J.C.S., 1873, 26, 575) will detect 1 mg. NaOAc (in a pure solution) and is thus more sensitive than the $FeCl_3$ or odour tests. A solution of 2$M$-$CuCl_2$–2$M$-NaCl is employed. If other acids are present, those with insol. Ag salts are first removed by adding 0·5$M$-$AgNO_3$, and $M$-$CaCl_2$ is added to ppt. Ag˙ and F′; the solution is then made alkaline, evaporated, and neutralised. $ClO_3'$ if present is first reduced by $KNO_2$; $NO_2'$ is oxidised by $HNO_3$. If tartrate is present, $H_2SO_4$ is added and AcOH distilled off and collected; if borate is present, Na K tartrate is added to give a non-volatile complex before distilling the AcOH. The solution is finally boiled with the $CuCl_2$ solution. Procedure in each case is described in detail. E. W. W.

**Micro-determination of lactic and carbonic acids.**—See this vol., 768.

**Colour reactions of organic acids.** R. C. Lopez (Biochem. Z., 1936, 284, 365—366).—Application of the $C_5H_5N$–$Ac_2O$ reaction (A., 1935, 1516) to various org. acids and their esters is described. F. O. H.

**Methods of determining organic acids.** E. V. Saposhnikova and R. P. Urinson (Bull. Appl. Botany U.S.S.R., 1934, Ser. 3, No. 5, 255—272).—Modifications of the Hartmann and Hillig method of determining oxalic, citric, and tartaric acids are given. Ch. Abs. ($e$)

**Precipitation of cystine by phosphotungstic acid.** M. Damodaran and T. G. Sivaswamy (Biochem. J., 1936, 30, 750—752).—The extent of pptn. of cystine (I) by 24-phosphotungstic acid at any particular temp. is dependent on the concn. of (I). It is not complete at any concn., and below a certain min. val. no pptn. takes place. At the concn. of (I) usually present in protein hydrolysates only a small fraction is pptd. J. N. A.

**Colour reaction of histamine and complex salts of heavy metals with methylglyoxaline.** F. Axmacher (Biochem. Z., 1936, 284, 339—342).—Aq. histamine and $CuSO_4$ give a dark blue colour, modifications of which by treatment with oxidising and reducing agents, acids, and alkalis are described. Co salts give a brown colour (cf. Zimmermann, A., 1930, 648). Methylglyoxaline gives cryst. complex *salts* with Cu, Co, and Ni [*e.g.*, $Cu(C_4H_6N_2)_6SO_4$; $Co(C_4H_6N_2)_6(NO_3)_2$]. F. O. H.

**Test for thymine: keto-enolic type of diazo-test.** G. Hunter (Biochem. J., 1936, 30, 745—749).—Thymine (I) coupled with diazotised sulphanilic acid in $Na_2CO_3$ solution gives an intense red colour when treated with NaOH and $NH_2OH$. $<$0·01 mg. of (I) can be detected; the test is not given by uracil or cytosine. The conditions for the "keto-enolic type" of diazo-test given by glucose, $CH_2Ac{\cdot}CO_2H$, MeCHO, $COMe_2$, tyrosine, and (I) are ($a$) capacity for keto-enol tautomerism and ($b$) the presence of a reducing agent for the development of colour. J. N. A.

**Colour reaction of certain nitro-compounds.** P. K. Bose and S. Ram (J. Indian Chem. Soc., 1935, 12, 687—689).—The colours (varying from cherry-red to indigo-blue) given by a no. of aromatic $o$-$NO_2$-compounds in EtOH with uric acid–$H_2O$–KOH at 25° and 100° are recorded. H. G. M.

**Detection of benzidine and tolidine present together.** L. Kulberg (J. Gen. Chem. Russ., 1935, 5, 1754—1756).—A drop of 10% aq. $CuSO_4$ and a drop of 10% aq. $KNO_3$ are placed on filter-paper, and a drop of the solution is added, when the spot turns blue in presence of $o$-tolidine (I), whilst benzidine (II) gives a brown ring with a blue centre. If the (II) contains $\nless 1\%$ of (I), the ring is green, and if the (I) contains $\nless 1\%$ of (II) the spot has a colourless centre, and a blue ring with a rose-red margin. R. T.

**Determination of small quantities of benzoic acid.** E. B. JOHNSON (J.S.C.I., 1936, 55, 109—110T).—The BzOH is first nitrated, then reduced by Zn to $m$-$NH_2 \cdot C_6H_4 \cdot CO_2H$, diazotised, and coupled with $\beta$-$C_{10}H_7 \cdot OH$ in alkaline solution. The bright red shade produced is matched with an aq. solution of Azogeranine B previously standardised for known amounts of $NH_2 \cdot C_6H_4 \cdot CO_2H$, and the amount of BzOH obtained by reference to curves. Alternatively, $\alpha$-$C_{10}H_7 \cdot OH$ may be used for coupling; in this case Neolan Pink B is employed. The method can be used in artificial light.

**Analytical uses of Nessler's reagent. Detection of aldehydes. Determination of glucose. I.** M. GOSWAMI, H. N. DAS-GUPTA, and K. L. RAY (J. Indian Chem. Soc., 1935, 12, 714—718).—Alkaline Nessler's solution is reduced by aldehydes (except OH-aldehydes in which OH is unprotected) but not, contrary to Bougault *et al.* (A., 1922, ii, 666, 709), by ketones (OH-ketones excepted). The extent of the reduction by glucose (I) and fructose depends on the strength and nature of the alkali (NaOH, KOH, or $Na_2CO_3$) and on the temp. Details for the determination of (I) are given. H. G. M.

**Bromide–resorcinol reaction. Reactions characteristic of phenols, opium alkaloids, and oxalic acid.** M. PESEZ (Bull. Soc. chim., 1936, [v], 3, 676—681; cf. A., 1935, 961; B., 1935, 828).—The colour reactions of tartaric acid and $CCl_3 \cdot CHO$ in presence of KBr, $H_2SO_4$, and $m$-$C_6H_4(OH)_2$ are traced to the intermediate formation of $CHO \cdot CO_2H$. A reagent containing this substance is obtained by reducing 5% $H_2C_2O_4$ solution with Al–Hg, filtering, and adding a few drops of conc. $H_2SO_4$ to the filtrate. Its use in the characterisation of phenols and phenolic acids is described. It can be employed in the differentiation of the chief opium alkaloids; $CCl_3 \cdot CHO$ in $H_2O$ (2 : 10) can also be used but gives less intense colours. $H_2C_2O_4$ is detected by reduction with Hg–Al and treatment of the reduced solution with conc. $H_2SO_4$ and $m$-$C_6H_4(OH)_2$ whereby a blue colour is developed, whereas $HCO_2H$, AcOH, BzOH, lactic, citric, tartaric, salicylic, and uric acids, $COMe_2$, glycerol and the products of its oxidation give yellow-orange to red-brown colours. H. W.

**Colour reaction for rotenone.** R. S. CAHN and J. J. BOAM (Chem. and Ind., 1936, 384).—The HCl–$HNO_3$–$CHCl_3$–thymol test for rotenone (B., 1936, 467) is untrustworthy, since it depends more on the presence or production of $HNO_2$ than on that of $HNO_3$. Pure $HNO_3$ gives the colour only very slowly. R. S. C.

**New reaction of opium alkaloids and its application to the detection of certain oxidising agents.** M. PESEZ (Bull. Soc. chim., 1936, [v], 3, 675—676).—A small quantity of the alkaloid or its salt is dissolved in 0·5 c.c. of 90—95% EtOH and treated with 1·5 c.c. of conc. $H_2SO_4$. After agitation the mixture is heated for 2—3 min. on the water-bath, cooled, and cautiously diluted with 5 c.c. of $H_2O$. The solution gives an orange-red colour with NaOCl which is not discharged by $SnCl_2$; Br–$H_2O$ and $NaNO_2$ give red colours. The reaction is positive with morphine, *apo*morphine, codeine, and their derivatives, negative with narceine and papaverine. Brucine and adrenaline give brown colours. Conversely, a stable reagent is obtained with codeine which affords a very sensitive test for NaOCl, Br–$H_2O$, and $NaNO_2$ but gives negative results with $NO_3'$, $ClO_3'$, $SO_4'$, $H_2O_2$, and metallic peroxides. H. W.

**Phthalic acid as reagent for optical identification of some metals and alkaloids.**—See this vol., 695.

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## Biochemistry.

**Variations of the respiratory quotient of the frog and the turtle as a result of sharp changes of the temperature of the environment.** L. DONTCHEFF and C. KAYSER (Compt. rend. Soc. Biol., 1936, 121, 1456—1458).—The R.Q. rises or falls with the temp.; the variations have no metabolic significance, but represent the variations of retention of $CO_2$ with temp. R. N. C.

**Respiratory quotient of the fasting frog and turtle maintained at 20°, 10°, and 5°.** L. DONTCHEFF and C. KAYSER (Compt. rend. Soc. Biol., 1936, 121, 1453—1455).—The R.Q. is unaffected by temp. within the above limits. R. N. C.

**Reticulocyte response in guinea-pigs following oral administration of certain antianæmic substances.** D. K. MILLER and C. P. RHOADS (New England J. Med., 1935, 213, 99—101).—Effects of a concentrate of rice polishings and autolysed yeast extract are examined. CH. ABS. (*p*)

**Action of sub-hæmolysing doses of mercuric chloride on the permeability of the erythrocyte.** M. ROCHA E SILVA (Compt. rend. Soc. Biol., 1936, 121, 1125—1128).—The permeability is unaffected. R. N. C.

**Forensic detection of blood.** O. SCHMIDT (Deut. Z. ges. gerichtl. Med., 1935, 24, 419—424; Chem. Zentr., 1935, ii, 1223).—Fusion of hæmin with resorcinol (cf. Schumm, A., 1928, 1263) and PhOH yields compounds with characteristic absorption spectra. H. N. R.

**Determination of bilirubin in blood.** A. VÁZQUEZ, V. G. ALVAREZ, and E. MATHET (Arch. med. cir. esp., 1933 [July 26]).—To 1 c.c. of serum is added a solution (1 : 1000) of methylene-blue (I) until the green colour first appearing turns blue. 0·01 c.c. of (I) is equiv. to $5 \cdot 6 \times 10^{-8}$ g. of bilirubin. CH. ABS. (*p*)

**Buffering power of hæmoglobin denatured by heat.** H. NAGAOKA (J. Biochem. Japan, 1936, 23, 101—123).—Hæmoglobin (I), when heated at its isoelectric point in isotonic aq. KCl, denatures first in a sol. condition before mol. aggregation occurs, a certain parallelism existing between increase in buffering power and denaturation. At higher temp., the buffering power and $O_2$ capacity decrease, the latter being a more exact criterion of the extent of denaturation. The change in $p_H$ of (I) on heating at 52° for several hr. is only +0·02. Diminution of buffering power, due to denaturation, occurs during the prep. of (I). F. O. H.

**Hæmatological studies in Indians. I. Hæmoglobin determination methods.** L. E. Napier and C. R. Das Gupta (Indian J. Med. Res., 1935, 22, 809—825).—Hellige's method can be adapted for clinical purposes if the colour standard, tubes, and pipettes are first checked by an abs. method of hæmoglobin determination. R. N. C.

**Solubility of hæmocyanins in saline solutions and specificity.** A. Roche and J. Roche (Compt. rend. Soc. Biol., 1936, **121**, 1512—1514).—The solubilities are similar to those of globulins, but the limiting concns. of $(NH_4)_2SO_4$ for pptn. vary with the species. R. N. C.

**Fractional ultrafiltration of the hæmocyanin of the snail.** P. Grabar (Compt. rend. Soc. Biol., 1936, **121**, 1472—1474).—The end-point of ultrafiltration occurs with membranes of mean pore diameter 86 $m\mu$. R. N. C.

**Specificity of the characters of the serum-proteins in different animals.** L. Samuel (Compt. rend. Soc. Biol., 1936, **121**, 1514—1516).—The specificity shows itself in the no. of different globulin fractions and their zones of pptn. Slight variations are often found even in members of the same species. The albumin–globulin ratio can be considered only as an "index." R. N. C.

**Function of serum-proteins.** R. Bierich, A. Lang, and A. Rosenbohm (Biochem. Z., 1936, **284**, 329—338).—Serum-albumin-I and -II [separated by fractional pptn. with $(NH_4)_2SO_4$] are respectively increased and decreased by addition to the serum of isamine-blue, pyronine, bile acids, or porphyrin; that of azelaic or sebacic acid and, in some cases, extracts of -II from pathological serum, has the reverse effect. The significance of the phenomenon in disease is discussed. F. O. H.

**Changes in serum-proteins in cancer.** R. Bierich and A. Lang (Biochem. Z., 1936, **248**, 443—447).—Neither the Cu-electrode potential method of Ettisch *et al.* (A., 1931, 503) nor the determination of acid groups indicates any differentiation between the globulin, albumin-I and -II (cf. preceding abstract) of normal and of cancerous blood. The tryptophan content of albumin-II, however, is diminished. F. O. H.

**Amino-groups of the proteins of human serum. Action of formaldehyde and ninhydrin.** W. L. Dulière (Biochem. J., 1936, **30**, 770—772).—Serum contains an average of 0·635 mg. of $NH_2$-N (determined by $CH_2O$ titration) per 100 mg. of dry protein, the albumin containing > the globulins. The purification and properties of the reaction products of the proteins with $CH_2O$ and ninhydrin are described. The ninhydrin–protein products do not react with $CH_2O$. J. N. A.

**Presence of serum-vitellin in vertebrate blood.** M. Laskowski (Biochem. Z., 1936, **284**, 318—321).—Data are given for the lipin-, phosphoprotein-, and acid-sol. P in the blood of various species of birds, reptiles, amphibia, and fishes during resting and spawning periods. F. O. H.

**Zinc–ferrocyanide deproteinisation and the nitrogen compounds of the plasma.** M. Paget and G. Guyader (Compt. rend. Soc. Biol., 1936, **121**, 1105—1106).—The reagent (I) does not adsorb urea or $NH_2$-acids, but retains a variable fraction of the uric acid (II). The difference between total N of the $CCl_3{\cdot}CO_2H$ and (I) filtrates is slightly > the polypeptide-N (difference between N of $CCl_3{\cdot}CO_2H$ and phosphotungstate ppts.), but if allowance is made for retention of (II), the N of the filtrate is of the order of that of the phosphotungstic acid filtrate. The (I) filtrate can be used for determination of the tyrosine index. R. N. C.

**Xanthoproteic reaction: its application to the determination of the tyrosine index of serum-polypeptides and of blood-phenols.** R. Lefaux (J. Pharm. Chim., 1936, [viii], **23**, 437—445; cf. A. 1936, 356).—The colour of the phosphotungstic acid filtrate ∝ the phenol content and is expressed as the "phenol index." E. H. S.

**Methyl derivatives of guanidine in blood: solitary and renal hypertension.** M. Zappacosta (Boll. Soc. ital. Biol. sperim., 1935, **10**, 705—708).—Methylguanidines are determined in blood colorimetrically with $\alpha$-$C_{10}H_7{\cdot}OH$ after adsorption on C in alkaline solution. They are increased in hypertension, but the increase is not ∝ the degree of hypertension or renal retention. R. N. C.

**Fatty acids of ox blood.** T. W. Parry and J. A. B. Smith (Biochem. J., 1936, **30**, 592—598).—The fatty acids (70% yield) consisted of 26% of saturated acids (10% of $C_{16}$, 13% of $C_{18}$, and 3% of higher acids) and 69% of unsaturated acids (including 26% of $C_{18}$, of which approx. 20% was oleic and 6% linoleic, 33% of $C_{20}$, and 10% of $C_{22}$). Neither linolenic nor any liquid saturated acid could be detected. W. O. K.

**Micro-determination of blood-fat.** L. Pollak (Mikrochem., 1936, **19**, 190—193).—0·1 c.c. of blood is treated with $EtOH+Et_2O$, and the fat is saponified with NaOH. Fatty acids are liberated by acidifying with $H_2SO_4$, and are extracted with light petroleum. The latter is removed and the acids are oxidised at 124° by 0·1$N$-$K_2Cr_2O_7$ in 90% $H_2SO_4$, excess of $K_2Cr_2O_7$ being determined iodometrically. J. S. A.

**Colour reaction of hexoses and their polymerides and its application to colorimetric determination of glucose in blood.**—See this vol., 709.

**Blood-sugar of anodonts.** M. Florkin and G. Bosson (Compt. rend. Soc. Biol., 1936, **121**, 1348—1350).—The "true" blood-sugar of anodonts is about 0·20—0·80 mg. per c.c., vals. being the same whether the blood is drawn from the heart or the palleal sac. Non-fermentable reducing substances are increased by fasting for a year. R. N. C.

**Determination of copper in plasma and blood-cells by Warburg's cysteine oxidation method.** J. Bjerrum and V. Henriques (Skand. Arch. Physiol., 1935, **72**, 271—282).—The method gives results comparable with those obtained by Macfarlane's colorimetric method. In a normal rabbit the blood-Cu was about equally divided between plasma and cells. After intravenous injection of Cu salts there was a marked rise in plasma-Cu followed by a slow fall during which the cell-Cu rose until both plasma- and cell-Cu reached the same level, after which both fell to normal. Nutr. Abs. (*m*)

**Helium solubility in blood at increased pressures.** J. A. Hawkins and C. W. Shilling (J. Biol. Chem., 1936, **113**, 649—653).—Solubility coeffs. of He in dog's blood equilibrated at atm. pressure varied from 0·083 to 0·089, and in ox blood from 0·080 to 0·091. The amount of He dissolved by whole blood under pressures of He of 1—6 atm. ∝ pressure. J. N. A.

**Determination of traces of ferric iron, as in blood-serum.** J. Dubnoff and P. L. Kirk (Mikrochem., 1936, **19**, 194—207).—Fe$^{III}$ in the CCl$_3$·CO$_2$H filtrate of serum is titrated by a differential potentiometric method with TiCl$_3$ in presence of KCNS. The use of standardised additions of KCNS and conditions of working is essential owing to slow reduction of Fe$^{III}$ by KCNS. J. S. A.

**Iron. X. Acid-soluble iron of plasma.** G. Barkan (Z. physiol. Chem., 1936, **239**, 97—108; cf. this vol., 109).—In human and horse blood the spontaneous transfer of Fe from corpuscles to plasma is not a diffusion; it is independent of hæmolysis and is unaffected by quinine and KCN but is generally restricted by CO. Transferred Fe is not adsorbed by Al$_2$O$_3$, whilst its ionisation by acids is not inhibited by CO. Plasma-Fe is usually reduced in experimental anæmias. W. McC.

**Determination of sodium in serum.** E. G. Ball and J. F. Sadusk, jun. (J. Biol. Chem., 1936, **113**, 661—674).—The method, based on the pptn. of Na as U Zn Na acetate, reduction of U$^{VI}$ to U$^{IV}$, and subsequent oxidation to U$^{VI}$ by K$_2$Cr$_2$O$_7$, is applicable to 0·2 c.c. of serum (error $< 1\%$). J. N. A.

**Determination of diastase in blood. I. Causes of error in Ottenstein's method.** F. Baltzer and J. Brinck (Klin. Woch., 1935, **14**, 929—930; Chem. Zentr., 1935, ii, 1223). H. N. R.

**Reduction of methylene-blue by the blood of young infants.** C. H. Smith (Amer. J. Dis. Children, 1935, **49**, 1189—1203).—The rate of decolorisation of methylene-blue by blood varies with age, and in presence of 3% aq. Na citrate is highest at $p_H$ 7·4—8·1 and does not occur at $p_H$ 6·3. The action is associated with erythrocyte constituents. Ch. Abs. (*p*)

**Heart-lung preparation with coagulable blood.** L. Brull (Compt. rend. Soc. Biol., 1936, **121**, 1351—1353). R. N. C.

**Hæmolytic action of photofluorescein.** J. F. Menke (Biol. Bull., 1935, **68**, 360—362).—Prep. of photofluorescein (I) by irradiation of Na fluorescein is described. (I) hæmolyses rats' blood in the dark, to the same extent as does fluorescein (II) in light. (II) has no action in the dark. Ch. Abs. (*p*)

**Existence of an optimum concentration of eosin for photodynamic hæmolysis.** M. Rocha e Silva (Compt. rend. Soc. Biol., 1936, **121**, 1122—1125).—The optimum concn. is 0·02—0·03%. R. N. C.

**Mechanism of anti-hæmolytic and -coagulatory action of blood-stabilising agents.** V. S. Iljin (Biochem. Z., 1936, **284**, 383—391).—Hæmolysis is inhibited by substances (*e.g.*, Na citrate, Ca$_2$C$_2$O$_4$, NaF, hirudin) which inhibit coagulation; the action of those pptd. by Ca$^{\cdot\cdot}$ is suppressed by Ca, Mg, Sr, and Ba chlorides, which, however, enhance hirudin etc. The phenomenon is not related to combination with blood-Ca. Addition of fresh serum re-initiates hæmolysis, indicating the participation of complement, whilst the inhibition of coagulation by citrate etc. is due to reaction with prothrombin, which is therefore related to complement (cf. A., 1927, 787). F. O. H.

**Anticoagulants. (A) Hypotensive action. (B) Effects of repeated injections. (C) Reciprocal action. (D) Effect of hypertensive and hypotensive substances on action of anticoagulants *in vivo*.** L. Robuschi (Boll. Soc. ital. Biol. sperim., 1935, **10**, 849—852, 852—856, 856—859, 860—864). R. N. C.

**Anticoagulant action of arsenobenzenes.** H. Goldie (Compt. rend. Soc. Biol., 1936, **121**, 1286—1290).—The anticoagulant power *in vitro* of sulpharsenobenzene (I) is $>$ that of novarsenobenzene (II) but the same *in vivo*. The min. anticoagulant dose of (I) *in vitro* is the same as the min. anti-alexic dose, suggesting that it inhibits a coagulant resembling alexin (possibly serozyme); the anticoagulant power of (II) is $>$ its anti-alexic power, and its action is inhibited by excess of cytozyme. (I) and (II), like other anti-coagulants, change the isoelectric point and pptn. characters of serum and plasma, but only in a narrow range of $p_H$. Arsenobenzene 606 exhibits only a feeble anticoagulant action, and is insol. at neutrality and toxic. R. N. C.

**Alexin and anti-alexic substances of horse serum.** H. Goldie (Compt. rend. Soc. Biol., 1936, **121**, 1282—1286).—The activity of alexin (I) in a hæmolytic system is increased by adding pseudoglobulins (II) to the hæmolytic serum before adding (I); (II) probably fix anti-alexins in the serum. R. N. C.

**Action of sucrose on alexin at high and low temperatures.** W. Mutsaars and J. Robert (Compt. rend. Soc. Biol., 1936, **121**, 1400—1402).—Sucrose protects alexin from inactivation at high but not at low temp.; this supports Madsen's view that the inactivation factors are different. R. N. C.

**Effect of sucrose on the thermo-resistance of alexin.** W. Mutsaars (Compt. rend. Soc. Biol., 1936, **121**, 895—897).—The thermo-resistance is increased. R. N. C.

**Minor hæmagglutinins. Blood containing autoagglutinin, heteroagglutinins, hæmolysins, and a rouleau-forming substance.** W. P. Belk (J. Lab. Clin. Med., 1935, 20, 1035—1042).—Data are obtained from the blood of a single patient recovering from mononucleosis. Ch. Abs. (*p*)

**High agglutinin content of the serum of an injurious universal donor.** M. Muller and E. Balgairies (Compt. rend. Soc. Biol., 1936, **121**, 1447—1449). R. N. C.

**Isohæmoagglutination and serum-albumins.** P. Michon, M. Vérain, and A. Ziégler (Compt. rend. Soc. Biol., 1936, **121**, 1419—1420).—Isohæmoagglutinins are contained in the serum-globulins, serin being inactive. R. N. C.

**Isohæmoagglutination and viscosity.** P. Michon, M. Vérain, and A. Ziégler (Compt. rend. Soc. Biol., 1936, **121**, 1417—1419).—Isohæmoagglutination is accompanied by a fall followed by a rise of $\eta$; the variations are detectable at dilutions > those where agglutination is detected, and do not occur in non-agglutinating systems. R. N. C.

**Isolation of antibodies by fixation on an adsorbent–antigen system with subsequent regeneration.** K. Meyer and A. Pic (Ann. Inst. Pasteur, 1936, 56, 401—412).—After adsorption of an antigen, the adsorbent–antigen complex will adsorb the corresponding antibody, the latter being eluted with 0·9% aq. NaCl at 60°. H. G. R.

**Titration of therapeutic sera by neutralisation of antibody *in vitro*.** L. Cotoni and J. Pochon (Compt. rend., 1936, **202**, 1121—1123).—The method is rapid and trustworthy and reveals differences not observed in the *in-vivo* method. W. McC.

**Antigenic power of glycogen and starch.** A. Giovanardi (Boll. Soc. ital. Biol. sperim., 1935, **10**, 777—780). R. N. C.

**Determination and calculation of the sensitisation of the complement-fixation reaction by titration with a fixed quantity of hæmolytic serum (anti-sheep hæmolytic system).** R. Crosnier (Compt. rend. Soc. Biol., 1936, **121**, 1306—1308). R. N. C.

**Viscosity of diphtheria toxin–antitoxin mixtures.** P. L. du Noüy and V. Hamon (Ann. Inst. Pasteur, 1936, 56, 359—375).—The increase in $\eta$ of a toxin solution on adding a small quantity of antitoxin may be used to standardise the latter. H. G. R.

**Mechanism of the variations of the Nicloux coefficient *k* in normal, hydrated, and dehydrated *Gobio fluviatilis*.** G. Fontès, J. Bruner, and A. Lindenberg (Compt. rend. Soc. Biol., 1936, **121**, 1458—1461).—Theoretical. R. N. C.

**Water impermeable to alcohol.** (A) G. Fontès. (B) M. Nicloux (Compt. rend. Soc. Biol., 1936, **121**, 1465—1470, 1470—1471).—Theoretical. R. N. C.

**Biochemistry of the vermiform appendix.** S. Sumida (J. Biochem. Japan, 1936, 23, 147—159).—Data are given for the physico-chemical properties, inorg. and org. constituents, and enzymes of the appendix juice (rabbit, dog) and for the $NH_2$-acid distribution in the proteins of the mucosa and muscle layers. F. O. H.

**Behaviour of thyroid follicles in the Harvey-Loomis centrifuge microscope.** J. F. McClendon (Science, 1936, 83, 283—284).—At a centrifugal force of $10^5$ to $2 \times 10^5 g$ the colloid from the thyroid follicules is extruded, and pptn. of thyroglobulin then occurs. The mechanism of this extrusion is detailed. L. S. T.

**Chemistry of helminths. III. *Taenia solium*. IV. *Diphylobotrium latum*. V. *Ascaris lumbricoides*.** I. A. Smorodincev and K. V. Bebeschin (J. Biochem. Japan, 1936, 23, 19—20, 21—22, 23—25).—Data are given for the dry wt., and contents of org. matter, ash, total N, and lipins of the worms, comparison being made between nematodes and cestodes. F. O. H.

**Chlorine content of feathers.** F. R. Dodd (Analyst, 1936, 60, 252—253).—Untreated feathers (mixed) contained 0·609% of Cl. After treatment (washing with boiling $H_2O$) the smaller grades (1—4) contained 0·051—0·085, and the larger (5 and 6) approx. 0·4%. The Cl, NaCl, and KCl contents of untreated feathers of several species are recorded. E. C. S.

**Iodine content of American fishery products.** E. J. Coulson (U.S. Bur. Fisheries, Invest. Rept., 1935, 1, No. 25, 7 pp.).—Of the fish tested (12 species fresh and canned) the highest vals. (parts per $10^9$) were found in the haddock (average 26,100) and the mullet (average 20,490). The average for codfish was 5350, and for canned Chinook salmon 2010. Of 8 fish meals shrimp had 23,080, crab 19,440, whitefish 12,080, and menhaden 4500. All the other vals. were between 1000 and 2000. The average vals. for fish oils were cod-liver oil 7670, salmon oil 1980, and sardine oil from Maine 470 and from California 260. Nutr. Abs. (*m*)

**Presence of acetone in beef.** A. Houdinière (Bull. Acad. vét. France, 1935, 8, 233—238).—Normal beef (muscle) contained 12 mg. of $COMe_2$ per 100 g. of tissue whilst in a heifer with milk fever 23 mg. were found. The $COMe_2$ was not removed by grilling but disappeared on prolonged boiling. Nutr. Abs. (*m*)

**Errors in the determination of ethyl alcohol in *Carassius auratus*.** G. Fontès, A. Lindenberg, and R. Gross (Compt. rend. Soc. Biol., 1936, **121**, 1461—1465).—The presence of other substances volatile in steam makes the method of Nicloux untrustworthy. R. N. C.

**Highly unsaturated alcohols in sperm-blubber oil.**—See this vol., 703.

**Decenoic acid, $C_{10}H_{18}O_2$, in sperm-head oil.**—See this vol., 705.

**Evolution of natural fats: a general survey.** T. P. Hilditch and J. A. Lovern (Nature, 1936, **137**, 478—481). L. S. T.

**Formation of adipocere.** Matzdorff (Deut. Z. ges. gerichtl. Med., 1935, 24, 246—249; Chem. Zentr., 1935, ii, 1197).—Adipocere appears in the fat cells of the hypodermis of the body of a new-born child kept for 7 days in flowing $H_2O$ at 11° temp. and 29° of hardness. R. N. C.

**Physico-chemical studies on lecithin.** H. B. Bull and V. L. Frampton (J. Amer. Chem. Soc., 1936, 58, 594—596).—Lecithin (I) prepared from egg-yolk by a modification of Sueyoshi's method (A., 1931, 975) contains a considerable amount of kephalin (II). Determinations of the isoelectric point (*P*) of various specimens of (I) by the electrophoretic method (A., 1935, 933) and extrapolation to zero concn. of (II), gives a val. of $p_H$ 6·4 for (I) (cf. Chain and Kemp, *ibid.*, 194). The *P* of (I) is lowered considerably by admixed (II); divergent results (lit.) are thus explained. When an aq. suspension of (I)+(II) is kept the *P* falls. Titration curves for such suspensions are reported. H. B.

**Presence and distribution of some reducing substances in brain tissue.** M. Mitolo (Atti R. Accad. Lincei, 1935, [vi], 22, 359—365).—Vals. are given of the reducing power (with respect to 2 : 6-dichlorophenol-indophenol) of different parts of the brain tissue of toads, rats, pigeons, guinea-pigs, rabbits, cats, sheep, horses, and oxen. O. J. W.

**Carbohydrates of muscle extracts of normal and diabetic dogs.** T. Cahn and J. Houget (Compt. rend., 1936, 202, 985—986; cf. this vol., 630). —Both normal and diabetic muscle extracts can polymerise glucose to glycogen, although the reaction is 30—40% slower in the latter case. P. G. M.

**Isolation of *dl*-arginine from kidney autolysate.** H. A. Heinsen (Z. physiol. Chem., 1936, 239, 162—164; cf. Ackermann, A., 1934, 874).—The lysine fraction (phosphotungstic acid ppt.) of the autolysate of ox-kidney yields *dl*-arginine (*disozoiodolate*, m.p. 201°). W. McC.

**Heat-denaturation of proteins as a chain reaction.** A. Fischer (Nature, 1936, 137, 576—577).—The denaturation of highly-purified serum-globulin by heat (70°) is a chain reaction, and the denaturation process may be due to the appearance of $\cdot NH_2$ or $\cdot SH$ on the surface of the spherical protein mols. L. S. T.

**Storage of proteins in the liver.** H. Li (Chinese J. Physiol., 1936, 10, 7—26).—Loss of blood, hunger, muscular activity, or phloridzin poisoning produces disappearance of protein from rat-liver cells. Feeding with vegetable or animal protein leads to storage of protein in the liver. J. N. A.

**Chemistry of rigor mortis.** I. A. Smorodincev and N. V. Nikolaeva (J. Biochem. Japan, 1936, 23, 27—39).—Cow's flesh, cooled to approx. 0° immediately after slaughter, contains equal amounts of myosin (I), myogen (II), and stroma, 70% of the total N being extractable by 0·65*M*-saline solution at $p_H$ 9·1. The extractability of (I) and (II) decreases to varying extents over a period of 24—48 hr. at 0° and then remains approx. const. Data for changes at 36° are also given and the bearing of the results on muscle-enzyme action and rigor is discussed. F. O. H.

**Structure and properties of "byssus" or silk of oysters.**—See this vol., 670.

**Porphyrins in the incubated bird's egg.** A. A. H. van den Bergh and W. Grotepass (Compt. rend. Soc. Biol., 1936, 121, 1253—1258).—The shell of the hen's egg contains protoporphyrin (I), which is secreted simultaneously with Ca albuminate by the uterine mucosa. (I) is synthesised from the white of the germinating egg, simultaneously with hæmoglobin (II). (I) is not a degradation product of (II), but probably an intermediate product in its synthesis. R. N. C.

**Uroporphyrin-III.** J. Waldenström (Z. physiol. Chem., 1936, 239, III—IV; cf. this vol., 503). —Isolation of uroporphyrin-III (from urine of acute porphyrinuria) prior to that by Mertens is claimed. The fæces in some cases contained coproporphyrin-I which, together with uroporphyrin-I, occurred in the urine. W. McC.

**Lipochrome of pig's liver.** L. Zechmeister and P. Tuzson (Z. physiol. Chem., 1936, 239, 147—148; cf. this vol., 499).—Fresh pig's liver contains about $3\times10^{-5}\%$ of lipochrome of which $\not> 2\times10^{-6}\%$ is carotene. W. McC.

**Surface tension of cow's milk.** G. Belle (Le Lait, 1936, 16, 13—30).—The $\gamma$ of milk produced in the Casablanca district averaged 50·4 dynes per cm. During the 3 hr. after milking, $\gamma$ decreased uniformly until it reached this const. val. The cooling of milk lowered $\gamma$ considerably, an average val. of 47·7 dynes per cm. being reached at 0°. W. L. D.

**Surface tension of milk.** W. Kopaczewski (Le Lait, 1936, 16, 356—359).—The $\gamma$ of various milk samples was very uniform, averaging 53 dynes per cm. Dilution with $H_2O$ does not change $\gamma$ appreciably. The $\gamma$ of separated milk differs only slightly from that of the corresponding whole milk; ageing of milk increases the val. by 2 dynes per cm. in 36 hr. Shaking milk for 5 min. increases $\gamma$ by 2 dynes per cm. W. L. D.

**Ammonia content of cow's milk.** M. Polonovski (Le Lait, 1936, 16, 232—234).—The average $NH_3$-N content of milk is 0·08%. The amount increases greatly on keeping or boiling. The increase on boiling is greater with old than with fresh milk. A low $NH_3$ content in condensed milk is an indication of efficient preservation. W. L. D.

**Effect of certain ingested fatty oils on the composition of cow milk fat.** T. P. Hilditch and H. M. Thompson (Biochem. J., 1936, 30, 677—691).— The milk fats from cows on winter diets supplemented with linseed or rape oils had higher oleic acid (I) contents; there was no evidence of the passage of the highly unsaturated linseed oil or the rape oil erucic ($C_{22}$) acids into the fat. With rape oil a decrease in the palmitic acid content occurred. Supplementing the diet with cod-liver oil caused a large reduction in the content of lower saturated acids, a large increase in that of (I), and a smaller increase in the $C_{20-22}$ unsaturated acids; palmitoleic acid was absent. By plotting the % of fully saturated glycerides against the % of saturated acids in the total acids in the control and test milk fats a straight line was obtained coincident with that obtained for animal depot fats (A., 1935, 645). The $C_{20-22}$ unsaturated acids are probably responsible for the sp. effect of cod-liver oil on lactating cows. H. D.

**Chemistry of cheese-ripening. III. Caseoglutin.** W. Grimmer and W. Lange (Milch. Forsch., 1936, **17**, 352—375).—The mixture of two caseoglutins in Tilsiter cheese, ripened for 10 weeks, was separated and each fraction sub-divided into 3 fractions with $COMe_2$: (1) insol. in $COMe_2$; (2) sol. in $COMe_2$, isoelectric point, $p_H$ 5·3; (3) sol. in $COMe_2$, isoelectric point, $p_H$ 7·0. The $NH_2$-acids of (1) showed a high content of leucine and proline. (3) contained only 0·05% of P, (1) and (2), 0·24—0·28%. W. L. D.

**Properties of milk-amylase and their modification by other milk constituents.** A. Schloemer (Milch. Forsch., 1936, **17**, 326—361).—$Pb(OAc)_2$, AcOH, and citric acid sera of milk are suitable for studying milk-amylase but the enzyme is adsorbed on caseinogen pptd. from milk by HCl. Amylolytic activity of milk is inhibited by dialysis. The enzyme can be reactivated by $CaCl_2$ and to a less degree by NaCl. The adsorption of amylase on the fat-caseinogen ppt. from milk and cream is greatest with high fat contents. A method of preparing the enzyme by dialysis of the Pb serum is described. W. L. D.

**Detection of narcotics, particularly barbituric acid derivatives, in various materials, especially cerebrospinal fluid and blood.** R. Fischer and O. Reisch (Z. ges. exp. Med., 1935, **95**, 739—753; Chem. Zentr., 1935, ii, 1223).—The drug (veronal, luminal, pernocton, medinal, dial, or evipan) is extracted with $Et_2O$ and sublimed. H. N. R.

**Humoral distribution of sodium chloride in blood and exudates.** G. dell' Acqua (Boll. Soc. ital. Biol. sperim., 1935, **10**, 765—768).—[NaCl] in normal pleural and abdominal exudates and articular or cutaneous blister liquids is $>$ that in serum, but $<$ that in purulent liquids. In cirrhotics, serum-NaCl is $<$ abdominal exudate-NaCl which is $<$ cerebrospinal fluid-NaCl. R. N. C.

**Lipase content of chyle. Absorption of digestive enzymes.** A. Kálló (Frankfurter Z. Path., 1935, **48**, 305—309).—Chyle collected before passage through any lymph gland in dogs and chyle from a human cyst contained lipase (I) probably absorbed from the intestine and contributing in part to the (I) content of lymph and blood. Nutr. Abs. (*m*)

**Chemical and physical constants of the body-fluid of sacculine crabs.** A. Drilhon (Compt. rend., 1936, **202**, 981—982).—In parasitised crabs the Ca, Mg, and protein contents of the lymph are $>$ normal. There are two isoelectric points, $p_H$ 6 and 8; the lymph of normal crabs has only one at $p_H$ 6. P. G. M.

**Biliary sugar.** G. Baltaceano and C. Vasiliu (Compt. rend. Soc. Biol., 1938, **121**, 1114—1116).—Biliary sugar is partly free and partly combined with proteins, and is related to blood-sugar. The content of sugar (especially that combined with protein) in bile from the gall-bladder is $>$ that in bile from the duct. R. N. C.

**Ultra-violet spectrum of hæmoglobin derivatives and bile pigment.**—See this vol., 662.

**Relation between blood-sugar and exocrine pancreatic function.** C. O. Hebb (Arch. internat. Pharmacodyn., 1935, **52**, 33—47).—In rabbits close parallelism exists between the lipase (I) content of the pancreatic juice and blood-glucose. Injection of glucose (II), but not of isotonic aq. NaCl, $NaHCO_3$, or sucrose, caused an increase in (I) concn. This effect was not altered by adrenalectomy, but was abolished by atropine. During hyperglycæmia (II) was excreted in the juice, but atropine did not affect this excretion. Nutr. Abs. (*m*)

**Blood-sugar concentration and the external secretion of the pancreatic gland.** B. P. Babkin (J. Amer. Med. Assoc., 1935, **105**, 1659—1662).—A close relationship exists between blood-sugar and secretion by the pancreas. Hyperglycæmia always increased the output of enzymes from the acinous cells. Insulin hypoglycæmia lowered the concn. of enzymes in the pancreatic juice, this effect disappearing after vagotomy. Nutr. Abs. (*m*)

**Indoluria.** J. C. Forbes and R. C. Neale (J. Lab. Clin. Med., 1935, **20**, 1017—1024).—Indole is not found in normal urine, but occurs in various diseases. Ch. Abs. (*p*)

**Simple, sensitive reaction for bilirubin in urine.** A. W. J. H. Hoitink (Nederl. Tijds. Geneesk., 1935, **79**, 2928—2930; Chem. Zentr., 1935, ii, 1224).—A modification of Fouchet's method (A., 1918, ii, 415). H. N. R.

**Unsaponifiable fraction of rat's fæces.** E. Ammundsen (Biochem. Z., 1936, **284**, 313—317).—With fæces of rats on either dried milk or meat diets, the sterols are approx. 40% unsaturated (Br method), whilst the solubility of the digitonide in MeOH is the same and slightly $>$ that of pure coprosterol (I). The unsaponifiable fraction on chromatographic analysis or distillation in a high vac. yields cetyl alcohol and a cryst. substance. The accuracy of determinations of (I) and dihydrocholesterol in their mixtures by the method of solubility of digitonides in MeOH is influenced by presence of $H_2O$, but not of $COMe_2$ or digitonin impurities. F. O. H.

**Effect of adrenalectomy on the colloidal state of [frog] muscle-proteins.** G. Benetato and R. Oprean (Compt. rend. Soc. Biol., 1936, **121**, 1551—1552).—The " solubility " of the proteins is reduced. R. N. C.

**Effect of adrenalectomy on the $p_H$ and buffering power of muscle.** G. Benetato (Compt. rend. Soc. Biol., 1936, **121**, 1547—1550).—$p_H$ and the buffering power in dogs are reduced. R. N. C.

**Anæmia of premature infants. II. Blood-iron and -hæmoglobin.** A. F. Abt (Amer. J. Dis. Children, 1935, **49**, 1204—1218).—The blood-Fe of premature and full-term infants is similar at birth and tends to decrease at similar rates to a min. at the 12th week. The types of curves for Fe and hæmoglobin (I) are similar, but vals. for premature infants reach the lower levels at corresponding age periods. The ratio % (I)/% Fe is the same as for full-term infants. Ch. Abs. (*p*)

**Iron content of teeth of normal and anæmic rats.** S. Ratner (J. Dent. Res., 1935, **15**, 89—92).—

The Fe content of the upper incisors of anæmic rats was 0·0082—0·0251% (average 0·0144). After removal of hæmoglobin-Fe the average content was 0·0126%. The corresponding vals. for healthy rats were 0·0280—0·0308% (average 0·0298; after removal of hæmoglobin-Fe 0·0262). A rough correlation seemed to exist between colour depth of the teeth and Fe content. NUTR. ABS. (*m*)

**Agranulocytic angina. Effects of toxic products of certain bacteria recovered from human stools and blood on the leucocytes of animals.** W. M. HARRIS and H. J. SCHATTENBERG (J. Lab. Clin. Med., 1935, **20**, 1053—1062).—Effects of toxic filtrates of cultures of *Clostridium welchii*, *Staphylococcus aureus*, *Salmonella enteritidis*, and *Streptococcus hæmolyticus* from an affected patient are examined. CH. ABS. (*p*)

**Serum-calcium in arthritis.** E. F. HARTUNG and C. H. GREENE (J. Lab. Clin. Med., 1935, **20**, 929—934).—Vals. were normal in rheumatoid arthritis but low in osteoarthritis. CH. ABS. (*p*)

**Calcium and phosphorus metabolism in generalised diseases of bones.** D. HUNTER (Proc. Roy. Soc. Med., 1935, **28**, 1619—1638).—In hyperparathyroidism blood-Ca is high (12·6—23·6 mg. per 100 ml.), plasma-inorg. P is low (1·0—2·7 mg.), and urinary Ca is greatly increased. Results are somewhat similar in some cases of generalised osteoporosis with renal glycosuria, but here there is a much smaller increase in serum-Ca in relation to the increased urinary Ca. In focal osteitis fibrosa, exophthalmic goitre, and Paget's disease the blood-Ca and -P levels are normal. In exophthalmic goitre Ca excretion may be greatly increased. Urinary Ca is generally raised in Paget's disease and is normal in focal osteitis fibrosa. In multiple myelomatosis high serum-Ca vals. associated with increased Ca excretion are usually found. If renal insufficiency is also present the plasma-P is high. Secondary carcinomatous deposits in bones may result in a negative or positive Ca balance. In osteomalacia there is nearly always a decreased level of serum-Ca accompanied by a high fæcal and low urinary output of Ca. NUTR. ABS. (*m*)

**Physico-chemical characteristics of body fluids in cancer patients.** G. J. GONZALEZ (Arch. med. cir. espec., 1933, No. 654).—Surface tension, sp. refraction, $\eta$, and cholesterol content of the blood are increased: electrical conductivity, glycæmia, and Ca content are lowered. Basal metabolism may increase initially but diminishes with the progress of the disease. Blood-$p_H$ decreases. CH. ABS. (*p*)

**Cancer. II. Determination of hydrogen-ion concentration of tissues in living animals by means of the capillary glass electrode.** C. VOEGTLIN, H. KAHLER, and R. H. FITCH (Nat. Inst. Health Bull., 1935, No. 164, 15—27).—Apparatus and technique are described. CH. ABS. (*p*)

**Gelation of serum-proteins in cancer.** W. KOPACZEWSKI (Compt. rend., 1936, **202**, 990—992).—The acceleration of gelation of serum-proteins in cancer cannot be correlated with the indices of neoformation of the globulins and myxoproteins.

P. G. M.

**Carcinogenic action and absorption and fluorescence spectra of 1 : 2-benzpyrene.**—See this vol., 664.

**Iron metabolism in cancer.** J. ROMHÁNYI and M. SCHMIDT (Frankfurter Z. Path., 1935, **48**, 380—385).—In rats on which "Putnoky–Ehrlich" carcinoma has been grafted, growth of the tumour was accompanied by an initial fall of 33% in the Fe content of the liver, followed by an increase to 14% < normal. Tumour-Fe was const. throughout its growth. The Fe content of the spleen decreased about 14%, whilst there was a 31% increase in that of the kidneys. The excretion of Fe by kidney and bowel decreased 10% and 14%, respectively.

NUTR. ABS. (*m*)

**Composition of normal and diseased organs. I. Normal, carcinomatous and sarcomatous lung.** B. LUSTIG (Biochem. Z., 1936, **284**, 367—375).—Data for the contents of N, P, lipins, sterols, carbohydrate, and protein- and residual N are given. Increased contents of albumose and peptone in sarcomatous and of non-reducing and nucleal carbohydrate in carcinomatous lung occur. F. O. H.

**Effect of various goitre-producing diets on growth of carcinoma, sarcoma, and melanoma in animals.** K. SUGIURA and S. R. BENEDICT (Amer. J. Cancer, 1935, **23**, 541—549).—Effects of goitrogenic diets with and without added I are compared. CH. ABS. (*p*)

**Complement fixation reactions in carcinoma.** H. W. LUNDY (J. Lab. Clin. Med., 1935, **20**, 923—929).—Fractionation of the phosphatide of cancer tissue by various solvents is described. The antigen involved in fixation with cancer sera was stable at 125°, but was destroyed by treatment with $C_5H_5N$ or $(CH_2{\cdot}NH_2)_2$. CH. ABS. (*p*)

**Effect of metabolic inhibitors on therapeutic irradiation of mouse tumours.** G. HARKER and W. MOPPETT (Austral. J. Exp. Biol., 1936, **14**, 15—25).—Injection of KCN, $KAg(CN)_2$, and $CH_2I{\cdot}CO_2Na$ increases the sensitivity of tumours to *X*-rays. The rate of destruction of $KAg(CN)_2$ in the tissues is much < that of destruction of KCN. The capability of organs to destroy KCN varies greatly, brain being most destructive by far. W. McC.

**Chemistry of crystalline humour, normally and in cataract.** M. PAGET and G. LEVIN (J. Pharm. Chim., 1936, [viii], **23**, 388—392).—In mammalian cataract the total ash, Ca, and cholesterol content of the cryst. humour are considerably, and that of S slightly, increased, whereas the K content is much decreased. J. S. A.

**Phosphorus compounds and bound sugars in the blood of diabetics.** M. MORIMUNE (Mitt. med. Akad. Kioto, 1935, **15**, 853—860).—In diabetes without complications the bound sugar and the acid-insol. P were increased, the vals. appearing to run parallel. The vals. for P in other forms were normal. In diabetes with complications the bound sugar, total P, glycerophosphate, and acid-insol P were increased whilst the ester-P was decreased. NUTR. ABS. (*m*)

**Immunity in diabetes. II. Relative importance of nutritional state and of blood-sugar level**

**in influencing development of the agglutinin after typhoid vaccine.** R. RICHARDSON (J. Clin. Invest., 1935, **14**, 389—392).—Rabbits with depleted liver-glycogen developed lower agglutinative titre after typhoid vaccine than did normal controls. No correlation was observed in diabetics between the fasting blood-sugar concn. and either the agglutinative titre developed after typhoid vaccine or the bactericidal power of the blood. CH. ABS. (*p*)

**"Donaggio reaction" in diabetes.** P. BIOCCA (Boll. Soc. ital. Biol. sperim., 1935, **10**, 737). R. N. C.

**Electrolyte balance in acute gout.** J. H. TALBOT, B. M. JACOBSON, and S. A. OBERG (J. Clin. Invest., 1935, **14**, 411—421).—Changes in $H_2O$ and salt metabolism occur during acute gout attacks. Before clinical or subject evidence appeared, there was diuresis accompanied by negative Na and Cl balances, and increased excretion of K, Ca, $NH_4$, titratable acid, $PO_4'''$, and urate. Metabolism of acute gout is not defined by uric acid alone. CH. ABS. (*p*)

**Leprosy: effect of vitamin-$B_1$-deficient diet on the incubation period of rat leprosy.** L. F. BADGER and W. H. SEBRELL (U.S. Publ. Health Repts., 1935, No. 50, 855—863).—The incubation period was shortened. CH. ABS. (*p*)

**Composition of lipomas.** E. STOLFI and G. STOLFI (Boll. Soc. ital. Biol. sperim., 1935, **10**, 742—744).—The fat of lipomas and that of the subcutaneous connective tissue are chemically essentially the same. R. N. C.

**Indole. IV. Indican–indole index of the blood in various experimental conditions. V. Indican–indole index of the blood in patients with normal liver and hepatic disease. VI. Microdetermination of free indole in blood.** E. MACCHIA (Boll. Soc. ital. Biol. sperim., 1935, **10**, 717—720, 720—722, 723—725).—IV. The index in the dog is scarcely changed by ligature of the renal peduncle, but is lowered by ligature of the hepatic peduncle and raised by removal of the intestine.

V. The index in normal patients is 10—16; it is reduced in hepatic disease, but increased in renal and intestinal affections.

VI. The serum is extracted with light petroleum + MeOH, and the extract washed with $H_2O$ (and with conc. NaOH if icteric). The solution is treated with a modified Ehrlich reagent, and, after evaporation of solvent, indole is determined colorimetrically in AcOH solution. R. N. C.

**Test for hippuric acid in diseases of the liver.** A. J. QUICK (Arch. Int. Med., 1936, **57**, 544—556).—Within 4 hr. of ingestion of 6 g. of NaOBz, approx. 3 g. of hippuric acid should be excreted. This val. is generally decreased in cases of hepatic disease. H. G. R.

**[Biological] synthesis of hippuric acid.** P. F. VACCARO (Surg. Gynecol. Obstet., 1935, **61**, 36—42).—Ingestion of NaOBz (5·9 g.) was followed by excretion of hippuric acid (3·5 g.) within 4 hr. Excretion was reduced in liver disease. CH. ABS. (*p*)

**Liver-lipase in pathology and therapeutics.** N. FIESSINGER and A. GAJDOS (Ann. Méd., 1935, **38**, 405—426).—The lipase (I) of serum is believed to be similar to and derived from hepatic (I) and to differ from pancreatic (I). Serum-(I) was diminished in cirrhosis and tumour of the liver. Persistent elevation of the serum-(I) in dogs followed injection of hepatic (I); in liver perfusion experiments the (I) content of the perfusate was increased. NUTR. ABS. (*m*)

**Thiocyanate treatment of mange in guinea-pigs.** E. B. CARMICHAEL (Science, 1936, **83**, 304).—A 2% solution of lauryl thiocyanate in cottonseed oil or a 5% aq. solution of "Loro" is effective. L. S. T.

**Virus ætiology of one form of lymphocytic meningitis.** G. M. FINDLAY, N. S. ALCOCK, and R. O. STERN (Lancet, 1936, **230**, 650—654).—The properties of a virus isolated from the cerebrospinal fluid of adults suffering from obscure symptoms associated with an increase of lymphocytes and its effect on various animals are described. L. S. T.

**Glycine treatment of progressive myopathic muscular atrophy and creatine balance.** L. PERRIA (Boll. Soc. ital. Biol. sperim., 1935, **10**, 751—752).—The action of glycine on creatine (I) balance is variable, and the (I) elimination curve shows no tendency to revert to normal. R. N. C.

**Creatine–creatinine excretion and the creatine content of muscle in nutritional muscular dystrophy.** T. G. NI (Chinese J. Physiol., 1936, **10**, 199—206; cf. Goettsch and Brown, A., 1932, 1057).—In muscular dystrophy caused by a special diet, the muscle-creatine (I) fell to a low level. In young guinea-pigs which had been fed the diet for some time, the urinary (I) increased, whilst creatinine (II) decreased. The early clinical symptoms of paralysis occurred some time after a significant rise in (I) and fall in (II). J. N. A.

**Phosphatase of biopsy tissue in progressive myositis ossificans.** W. E. WILKINS, E. M. REGEN and G. K. CARPENTER (Amer. J. Dis. Children, 1935, **49**, 1219—1221).—Fibrous tissue and muscle from the region of lesions in the preossification stage showed high phosphatase activity. Heterotrophic bone and cartilage from an older lesion showed activity > that of a normal rib. Vals for normal tissue were low. CH. ABS. (*p*)

**Indole and skatole content of the blood in kidney disease.** M. ZAPPACOSTA (Boll. Soc. ital. Biol. sperim., 1935, **10**, 708—710).—Blood-indole and -skatole are not increased in acute glomerular nephritis or nephrosis, but are moderately increased in renal sclerosis and uræmia, the increase being independent of the degree of injury. R. N. C.

**Effect of renal denervation on patients suffering from nephritis.** I. H. PAGE and G. J. HEUER (J. Clin. Invest., 1935, **14**, 443—458).—Renal denervation in acute nephritis diminished protein excretion in most cases. Urea clearance was unaffected. CH. ABS. (*p*)

**Neuritis in pregnancy successfully treated with vitamin-$B_1$.** G. W. THEOBALD (Lancet, 1936, **230**, 834—837). L. S. T.

**Polypeptidæmia in pellagra.** I. Ornstein and E. Vascauteanu (Compt. rend. Soc. Biol., 1936, **121**, 1440—1442).—Polypeptides generally show an increase which is not $\propto$ the fall of blood-cholesterol or to blood-urea. R. N. C.

**Diet of sunflower seeds for the study of experimental polyneuritis.** A. Allegri (Boll. Soc. ital. Biol. sperim., 1935, **10**, 839—943). R. N. C.

**Follicular hormone and pregnancy diagnosis in women and in the mare.** S. L. Sala (Rev. sudamer. endocrinol., 1935, **18**, 325—329).—Filtered urine (5 c.c.) is heated with 1 c.c. of HCl at 100° for 5 min., and after cooling is extracted with $C_6H_6$. After removal of $C_6H_6$ the residue of the extract is dissolved in $H_2SO_4$ (0·8 c.c.) and heated at 70—80° for a few min. Fluorescence, greenish by transmitted light, constitutes a positive test, which is trustworthy for mare's but not for human pregnancy. Ch. Abs. (*p*)

**Determinations of prolan and œstrin in pregnancy with special reference to late toxæmia and eclampsia.** G. van S. Smith and O. W. Smith (Surg. Gynecol. Obstet., 1935, **61**, 27—35; cf. this vol., 229).—A peak level of prolan (I) occurs in the 2nd—4th months of pregnancy. Œstrin (II) increases as pregnancy advances to term. In late toxæmia excess of (I) has probably been present for some time. Nausea in early pregnancy is associated with low (II). Neither (I) nor (II) is concerned in miscarriage. Ch. Abs. (*p*)

**Unsalted diet and pregnancy. Chlorine contents of erythrocytes and plasma and their relationship to alkali reserve.** G. Lambert (Zentr. Gynäkol., 1935, **59**, 2598—2601).—In pregnant women on ordinary diet there appeared to be no correlation between Cl index (cell-Cl : plasma-Cl) and alkali reserve. When the diet was poor in NaCl there was a slight decrease in cell- and plasma-Cl, but no change in the index or the alkali reserve. Nutr. Abs. (*m*)

**Mineral content of the silicotic lungs of an earthenware worker.** N. Sundius, A. Bygdén, and T. Bruce (Trans. Ceram. Soc., 1936, **35**, 167—181).—A method of extraction with $H_2O_2$ by which lung dust (I) may be isolated almost unchanged is described. In the (I) of the worker, which was fairly uniformly distributed in the lung, all the components of the raw materials were found, although some increase in the kaolinite and mica, and decrease in the flint-quartz and felspar contents, had resulted from separation by the air and the respiratory organs. The average diameter of most of the particles of the (I) was $< 2—4 \times 10^{-3}$ mm. Chemical and *X*-ray examination showed that the mineralogical composition of the (I) was essentially the same as that of factory dust of similar grain-size, and that the dust had undergone little or no decomp. in the lung. A. L. R.

***X*-Ray appearances of the lungs of electric arc welders.** A. T. Doig and A. I. G. McLaughlin (Lancet, 1936, **230**, 771—775).—Alterations in the tissues due to inhalation of the fumes produced are described. The probable composition of the fumes is discussed. L. S. T.

**Blood chemistry of about five hundred patients with common skin diseases.** H. Goodwin (J. Lab. Clin. Med., 1935, **20**, 1048—1052).—Blood-sugar and -NaCl were generally within normal range, but relatively high -NaCl was associated with relatively low -sugar and *vice versa*. Urea-N and uric acid were not appreciably changed. Ch. Abs. (*p*)

**Technique of the Bordet–Wassermann reaction in serum freed from the fraction precipitable by hydrochloric acid.** O. Auguste (Compt. rend. Soc. Biol., 1936, **121**, 1449—1450). R. N. C.

**Clinical value of prolan *A* determinations in tetroma testis.** M. Cutler and S. E. Owen (Amer. J. Cancer, 1935, **24**, 318—325).—Affected patients excrete increased amounts of prolan *A*. Ch. Abs. (*p*)

**Thyroid diseases and blood-chloride.** J. Decourt and C. O. Guillaumin (Compt. rend. Soc. Biol., 1936, **121**, 1332—1335).—Corpuscular and plasma-Cl, both absolutely and relatively, are slightly reduced in myxœdema and increased in Basedow's disease and experimental hyperthyroidism in the rabbit. R. N. C.

**Mandelic acid and ammonium mandelate in the treatment of urinary infections.** H. E. Holling and R. Platt (Lancet, 1936, **230**, 769—771).—Treatment with Na mandelate+$NH_4Cl$ or $NH_4$ mandelate rendered the urine sterile in 2—21 days. L. S. T.

**Cholesterol in xanthomatosis.** L. Nekám, jun., and B. Ottenstein (Klin. Woch., 1935, **14**, 641—643).—Cholesteryl esters and lecithin are increased, and free cholesterol (I) is decreased, in xanthomatosis. Addition of liver- or pancreas-pulp to a (I) emulsion does not cause (I) decomp. under sterile conditions. Xanthomatosis is not associated with a functional disturbance of (I) breakdown. R. N. C.

**Old age and basal metabolism.** F. G. Benedict (New England J. Med., 1935, **212**, 1111—1122).—Total metabolism per unit surface area and heat production per unit wt. have been determined in women of varying ages. Ch. Abs. (*p*)

**Growth and basal metabolism. IV. Changes in the basal metabolism of children during the year.** I. Nakagawa (Amer. J. Dis. Children, 1935, **49**, 1232—1239).—The total heat production of children aged 3—11 years increases by approx. 30 g.-cal. per day, and is expressed more satisfactorily by changes in wt. than by those in height or surface area. Ch. Abs. (*p*)

**Basal metabolism of male Chinese in Manchuria.** F. G. Benedict and H. S. D. Garven (Chinese J. Physiol., 1936, **10**, 141—146).—With 20 men, the average respiration rate was 15 and the $O_2$ consumption 208 c.c. per min. The average metabolism was 3·5% below the Harris–Benedict standard. J. N. A.

**Variations in the processes of ossification in relation to normal and experimentally-modified rates of growth.** G. Scoz and P. L. Marangoni (Boll. Soc. ital. Biol. sperim., 1935, **10**, 678—680).—Phosphatase (I) in the bones of the rat falls in winter,

whilst blood-(I) is unchanged; the ossification processes are retarded but not modified. Thyroxine (II) in low concns. lowers body-wt., bone-(I) and -Ca, and increases blood-(I), in dogs and guinea-pigs, whilst in rats it retards the rate of growth and reduces blood-(I) and bone-Ca. Following the effects of (II), the rate of growth and bone-Ca and -P increase whilst blood-(I) falls, the vals. returning to normal after 27 days. Repeated doses of (II) in the rat cause a rise in bone-(I) and a fall in -Ca and -P.
R. N. C.

**Adrenal capsules and gaseous metabolism. I. II. Effect of pilocarpine on gaseous exchange in decapsulated rats.** G. Michele (Boll. Soc. ital. Biol. sperim., 1935, **10**, 628—631, 631—633).—I. Gaseous exchange falls for the first few hr. after decapsulation, but rises again in animals surviving the following day; this does not support the hypothesis that the adrenal capsules control gaseous exchange by discharge of adrenaline.

II. Pilocarpine does not increase $O_2$ consumption, and hastens death. R. N. C.

**Oxidative metabolism in sea-urchins' eggs.** P. E. Lindahl and L. O. Öhman (Naturwiss., 1936, **24**, 157—158).—The action of KCN on the respiration of the fertilised eggs at various stages indicates that part of the respiration is not inhibited and is therefore not related to the Fe-containing respiratory enzyme. An increase in the velocity of $O_2$ transport in substrate activation is due to changes in the enzyme system. Other aspects (*e.g.*, the rôle of "carriers") of respiration are discussed. F. O. H.

**Formation of hydrogen cyanide and formaldehyde by oxidation of organic substances.**—See this vol., 707.

**Reduction intensity of living cells.** A. J. Kluyver and J. C. Hoogerheide (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 298—305; cf. A., 1934, 1138).—The reduction intensity of the living cell is only in a restricted sense a sp. property of the cell, and is determined at any moment by the nature of the metabolic processes in the cell. The oxidation–reduction potentials under well-defined metabolic conditions are characteristic for the reduction intensity of the cells if the medium contains a partly reduced redox system, capable of penetrating the cells. Vals. for $r_H$ of 8·4—9·0 are characteristic for the reduction intensity of all cells under the conditions of alcoholic fermentation, whilst for lactic acid formation the vals. are 5·0—6·0.
J. N. A.

**Bile secretion and a diet rich in liver.** G. Baltaceano and C. Vasiliu (Compt. rend. Soc. Biol., 1936, **121**, 1535—1537).—The diet increases bile secretion in the dog, but lowers cholesterol, acids, pigments, and inorg. substances, and $\eta$ and $n$ of the bile. R. N. C.

**Pancreas diet and the biliary function of the liver.** G. Baltaceano and C. Vasiliu (Compt. rend. Soc. Biol., 1936, **121**, 1537—1541).—During administration of pancreas diet to dogs, bile secretion is increased; elimination of bile salts (I), org. and inorg. substances is increased, pigment (II) elimination is reduced, cholesterol (III) shows slight variations that tend to increase, and $\eta$ and $n$ of the bile are unaffected. After cessation of the diet, bile secretion and the constituents oscillate for a period, after which (I), (III), and the dry residue of the bile fall, whilst (II) and $H_2O$ rise. R. N. C.

**Nitrogenous metabolism in Manchuria.** C. Wang (Chinese J. Physiol., 1936, **10**, 135—139).—Data are given for total, urea-, $NH_3$-, uric acid-, and creatinine-N in the urine of 32 men. J. N. A.

**Nitrogen metabolism in infants.** M. V. Miller-Shabanova (Acta paediat., 1935, **18**, 192—210).—The blood of fasting children aged 1 month to 2 years contained 1—5·3 g. of total N per 100 ml., increasing with age. The vals. in well-nourished were > in dyspeptic infants. The val. rose to a max. 3—4 hr. after a meal, the height of the max. depending on the amount of protein in the diet. The max. with breast milk was 1·4—4·7 g. per 100 ml., with mixed feeding 2·1—7·7, and with cow's milk 2·04—8·54. The fasting val. for non-protein-N was 6—16 mg. per 100 ml. After feeding, vals. of 17—20 mg. were obtained, the relationship to the protein of ingested food being insignificant. Nutr. Abs. (*m*)

**Rate of absorption of iodine and glycine from the gastro-intestinal tract in health and disease.** C. W. Heath and H. W. Fullerton (J. Clin. Invest., 1935, **14**, 475—481). Ch. Abs. (*p*)

**Perfusion of the stomach. XII. Perfusion with ornithine and citrulline.** K. Kitsugawa (J. Biochem. Japan, 1936, **23**, 131—138).—Citrulline (A, 1933, 172), perfused through the dog's stomach, produces both arginine and ornithine, the latter (as when directly perfused) being decomposed into arginine, $NH_3$, and urea. F. O. H.

**Renal excretion of creatinine in man.** J. A. Shannon (J. Clin. Invest., 1935, **14**, 403—410.—Increase in creatinine (I) in the plasma is associated with depression of (I) clearance, both abs. and relative to inulin clearance. Secretion of (I) by renal tubules is probable. Phloridzin brings the two clearances together by depressing tubular secretion of (I).
Ch. Abs. (*p*)

**Transformations of adenosinetriphosphoric acid in muscle. III. Isolated muscle.** D. Ferdmann, O. Feinschmidt, and M. Dmitrenko (Biochem. Z., 1936, **284**, 392—400; cf. A., 1935, 778).—Activity of isolated frog's muscle results in decomp. of adenosinetriphosphoric acid and concomitant formation of $P_2O_7''''$ in amounts ∝ the work done and the adenylic acid produced. Inosinetriphosphoric acid is not formed. F. O. H.

**Presence of strychine–barbituric complex in the urine of animals that have received separate injections of strychnine and barbituric acid.** V. de Lavergne, P. Kissel, Weiller, and H. Chahidi (Compt. rend. Soc. Biol., 1936, **121**, 1412—1413).—Both strychnine and barbiturate are found in alkaline $Et_2O$ extracts of the (guinea-pig's) urine after hydrolysis with $H_2SO_4$.

**Production of dihydroxydihydroanthraceneglycuronic acid from anthracene.**—See this vol., 721.

**Flavins and metabolism. III. Action of lactoflavin and methyl alcohol extract of liver on blood-glycolysis.** A. J. CHARIT, S. A. NEUFACH, and K. N. MOROZOVA. **IV. Seasonal changes in the flavin content of the liver in cattle. V. Effect of alloxan and thymonucleic acid in the diet on the flavin content of rats' liver.** A. J. CHARIT and N. V. CHAUSTOV (Compt. rend. Acad. Sci. U.R.S.S., 1936, **1**, 127—131, 177—180, 235—236).—III. Aërobic glycolysis in dog's blood is unaffected by addition of lactoflavin, which, however, greatly increases anaërobic disappearance of glucose without increasing lactic acid production. MeOH extract of ox liver does not affect anaërobic but intensifies aërobic glycolysis.

IV. Seasonal changes in the diet of cattle produce corresponding (sometimes very great) changes in the flavin (I) content of their livers (max. in summer, min. in spring). In men on meat diets liability to pellagra increases with decrease in (I) content of dietary liver.

V. Addition of 1 mg. daily of thymonucleic acid [possibly containing traces of (I)] to the diet of rats slightly increases the (I) content of their livers but that of alloxan does not affect the content.

W. McC.

**Carbohydrate metabolism of the liver. V. Sugar intake in the normal intact cat during glucose absorption. VI. Sugar output and intake in the daily digestive cycle.** C. TSAI and C. YI (Chinese J. Physiol., 1936, **10**, 87—102, 105—117; cf. A., 1934, 1251).—V. The glucose (I) content of the inflowing and outflowing hepatic blood in cats with permanent angiostomy cannulæ was studied before and at various intervals during (I) absorption. During the first 3 hr. of absorption, inflow (I) was always > outflow (I). The (I) intake by the liver reached a max. between 1·5 and 2·5 hr. and ceased at 4 hr. after administration of (I). The liver- and muscle-glycogen increased in animals fed with (I), probably due to glycogen formation during absorption of (I). The liver of the decapitated cat showed an output > the inflow.

VI. With alimentary hyperglycæmia, intake of (I) was often > output. A high portal (I) level was necessary for intake to be > output, but there was no relation between arterial (I) levels and the relative amount of intake. Ingestion of a pure meat diet had no effect on the relative concns. of (I) between inflowing and outflowing blood. With cessation of absorption the hepatic outflowing (I) was always > the portal and arterial (I). The liver appeared to discharge (I) into the circulation at a relatively const. rate during the entire interval between meals.

J. N. A.

**Carbohydrate metabolism. III. Relation of salt and water to the oxidation of glucose.** J. A. JOHNSTON and J. W. MARONEY (Amer. J. Dis. Children, 1935, **49**, 1240—1255; cf. A., 1935, 888).—Oxidation of glucose is accelerated by oral administration of acid salts ($NH_4Cl$, $CaCl_2$) and retarded by alkaline salts ($NaHCO_3$). It is depressed by NaCl and $H_2O$ while these are retained in the body, but increases subsequently. Following thyroxine administration glycogen stores are depleted, and acid salts then inhibit oxidation completely, whereas alkaline salts have the reverse effect. CH. ABS. (*p*)

**Activators of carbohydrate fission as water-soluble constituents of food.** H. VON EULER and M. MALMBERG (Biochem. Z., 1936, **284**, 455—460).—Addition of cryst. cozymase will not induce growth in rats fed on a vitamin-$B_4$-free diet; that of a yeast-juice prep. (inactive alone) together with nicotinamide induces significant growth. Fractions from extracts of nerve and brain-tissue have a similar action. The rôle of cozymase and other factors of carbohydrate metabolism in nutrition is discussed.

F. O. H.

**Nature of sugars in a theoretically complete and balanced diet; can they have any effect on the development and maintenance of the rat?** L. RANDOIN and S. QUEUILLE (Compt. rend. Soc. Biol., 1936, **121**, 1318—1323).—Growth and maintenance are normal with dextrin (I), sucrose, or maltose. Galactose and lactose exhibit toxic action. Glucose and fructose (II) produce normal growth, but maintenance is poor, particularly with (II), where loss of wt. occurs at maturity unless (I) is added.

R. N. C.

**Excretion of inulin, xylose, and urea by normal and phloridzinised man.** J. A. SHANNON and H. W. SMITH (J. Clin. Invest., 1935, **14**, 393—401).—Inulin (I) clearance in man after intravenous infusion is independent of plasma concn. (I) is not secreted by human renal tubules. Xylose and sucrose are normally reabsorbed by the tubules from glomerular filtrate. Evidence against reabsorption of (I) should be obtained before (I) clearance is accepted as a measure of glomerular filtration. CH. ABS. (*p*)

**Metabolism of fructose. VI. Influence of the level of ovarian function.** A. W. ROWE, M. A. MCMANUS and A. J. PLUMMER (J. Amer. Med. Assoc., 1935, **104**, 451—455).—Ovarian function has little influence (cf. A., 1934, 1393). CH. ABS. (*p*)

**Medical problems in mineral metabolism. I. Legacies of evolution. II. Sodium deficiencies in clinical medicine. III. Experimental human salt deficiency.** R. A. MCCANCE (Lancet, 1936, **230**, 643—650, 704—710, 765—768, 823—830).—Lectures.

L. S. T.

**Absorption of mineral substances by the embryo of *Sepia officinalis*.** S. RANZI (Atti R. Accad. Lincei, 1935, [vi], **22**, 605—608).—The embryo can absorb the following elements from sea-$H_2O$: Na, K, Ca, Mg, P, Cu, Fe, Mn, V, B, Li, Sr.

O. J. W.

**General application of Loeb's ionic quotient.** D. L. RUBINSTEIN, H. BURLAKOVA, and W. LVOVA (Biochem. Z., 1936, **284**, 437—442).—With changes in the nutrient media of *Drosophila*, the Na : Ca ratio of the organism can be varied between 300 and 1·6; the movements of the flies appear to be unchanged (cf. A., 1934, 1035; 1935, 1017). F. O. H.

**Ionic equilibrium between the aqueous humour and blood plasma of cats.** H. DAVSON, W. S. DUKE-ELDER, and G. H. BENHAM (Biochem. J., 1936, **30**, 773—775; cf. Walker, A., 1933, 849).—Determinations of Na, K, and Cl indicate the existence of a Donnan equilibrium between aq. humour and blood-plasma as far as these ions are concerned. The bearing of these results on the problem of glaucoma is discussed. J. N. A.

**Mechanism of the action of sodium chloride and bicarbonate in the maintenance of acid–base equilibrium.** A. Slatineanu, I. Balteanu, M. Sibi, M. Franche, and L. Cantacuzène (Compt. rend. Soc. Biol., 1936, **121**, 1423—1427).—$NaHCO_3$ rectifies acidosis in patients with increased corpuscle–plasma-Cl ratio, which is reduced to normal. Chloropenia with normal alkaline reserve is due to NaCl deficiency, whilst with reduced alkaline reserve it is due to Na deficiency and can be treated with $NaHCO_3$. R. N. C.

**Numerical analysis of Lars Spildo's investigations into the calcium metabolism of growing swine. Fæcal calcium elimination and calcium absorption.** A. Westerlund (Lantbruksögsk. Ann., 1935, **2**, 71—105).—The analysis (A., 1935, 1274) leads to the following conclusions. Ca : P ratio, vitamin-*D* intake, or acid–base balance had no effect on Ca excretion in fæces or Ca absorption. Both excretion and absorption of Ca were determined by Ca intake. With intakes of 2—5 g. per head per day there was no correlation between intake and fæcal excretion. Absorption increased with intake up to a max. at about 8 g. total intake, or about 0·5 g. per kg. body-wt. At this level % absorption was 60. Nutr. Abs. (*m*)

**Bromine metabolism in man.** P. Chatagnon and C. Chatagnon (Compt. rend., 1936, **202**, 1119—1120).—In manic-depressive insanity and similar diseases variations in blood-Br appear to depend on the intake of Br and on the Br : Cl ratio. There is no characteristic decrease in blood-Br and the Br content of the pituitary is not abnormally high (cf. Zondek *et al.*, A., 1933, 739). W. McC.

**Effects of low-phosphorus rations on growing pigs.** C. E. Aubel, J. S. Hughes, and H. F. Lienhardt (J. Agric. Res., 1936, **52**, 149—159).—Low-P rations induce lessened appetite, poor utilisation of food and storage of energy, inability to develop bone and muscle normally, decrease in blood-inorg. P, increased thirst, and corresponding urination. A. G. P.

**Comparative studies in the sulphur metabolism of the dog and pig.** J. A. Stekol (J. Biol. Chem., 1936, **113**, 675—682).—With dogs (but not pigs) on a protein-free diet, ingested *iso*barbituric acid readily yields ethereal sulphates in the urine, and the yield is increased by feeding in addition *l*-cystine, *dl*-methionine, cysteine, or $Na_2SO_4$. Like the dog, rabbit, and rat, the pig synthesises *p*-bromophenyl- and 1-α-naphthyl-mercapturic acids from PhBr and $C_{10}H_8$, respectively. J. N. A.

**Light and reproduction in game birds.** L. B. Clark, S. L. Leonard, and G. Bump (Science, 1936, **83**, 268).—Irradiation by a Mazda lamp stimulates growth in the reproductive organs of grouse, quail, and pheasants. L. S. T.

**Measures of radioactivity in zones of endemic goitre.** G. Pighini and O. Rülke (Boll. Soc. ital. Biol. sperim., 1935, **10**, 663—666).—Vals. of the ionising power of the air and $H_2O$ of a no. of Italian districts are given. R. N. C.

**Radioactivity, iodine, and the thyroid.** G. Pighini (Boll. Soc. ital. Biol. sperim., 1935, **10**, 661—663).—I protects the thyroid of the rat against changes due to consumption of $H_2O$ containing Rn. R. N. C.

**Physico-chemical properties and local anæsthetic action. (A) Surface tension, adsorption, and prevention of adsorption. (B) Flocculation of colloids and relative lipin-solubility.** C. Rohmann and B. Scheurle (Arch. Pharm., 1936, **274**, 225—235, 236—244).—(A) The anæsthetic efficiency of 12 compounds, $p$-$OR{\cdot}C_6H_4{\cdot}CO_2[CH_2]_x{\cdot}NEt_2$ (R=H or alkyl), is approx. parallel to the lowering of γ of their 0·05*M* solutions at $p_H$ 5·9 (less so at that $p_H$ which just prevents pptn. of free base) and to their efficiencies in preventing adsorption of glucose by C (" Verdrängungsadsorption "), but not to the amounts adsorbed on C. The parallelisms do not hold if $R{=}NEt_2{\cdot}[CH_2]_2$ nor for four other local anæsthetics.

(B) Better parallelism than that described in (A) exists between efficiency, ability to ppt. colloidal albumose, and lipin-solubility (measured by partition between $H_2O$ and $Et_2O$ at $p_H$ 7·3). Exceptions exist amongst substances of different classes. R. S. C.

**Limits of action of hydrogen-ion concentration on vasal tonus : lung preparation of the dog.** G. Russo (Boll. Soc. ital. Biol. sperim., 1935, **10**, 801—803).—The vessels dilate if $p_H$ is lowered 0·2 unit from 7·2, and contract if $p_H$ is raised by this val. R. N. C.

**Action of positive chemical stimuli on cultures *in vitro*. I. Benzene.** F. Guercio and R. Arnone (Boll. Soc. ital. Biol. sperim., 1935, **10**, 621—622). R. N. C.

**Embryonic "induction" by chemical substances.** M. W. Woerdeman (Proc. K. Akad. Wetensch. Amsterdam, 1936, **39**, 306—314). J. N. A.

**Cytological modifications of the hepatic cell through variation of the oxygen and carbon dioxide contents of the respired air.** M. Milletti (Boll. Soc. ital. Biol. sperim., 1935, **10**, 755—757). R. N. C.

**Effect of compressed air on animals. XVII. Combustion of ethyl alcohol injected into rats. XVIII. Combustion of ethyl alcohol injected in increasing doses.** A. Aggazzotti. **XV. Oxygen and carbon dioxide in the expired air of the rabbit subjected to the action of compressed air.** G. Bucciardi, M. Leonardi, and E. Ferrarini (Boll. Soc. ital. Biol. sperim., 1935, **10**, 782—784, 784—786, 787—788).—XVII. EtOH oxidation is depressed by exposure to compressed air.

XVIII. EtOH oxidation increases progressively with the quantity injected until a limit is reached at which it tends to remain const. ; it is always < that at atm. pressure.

XV. $CO_2$ production and $O_2$ consumption both increase with the pressure, the R.Q. remaining const. R. N. C.

**Action of calcium ions on the hypertension and hyperglycæmia due to potassium ions.** R. HAZARD (Compt. rend. Soc. Biol., 1936, **121**, 1036—1039).—$Ca^{\cdot\cdot}$ does not antagonise the action of $K^{\cdot}$ in increasing the secretion of adrenaline (I), but reduces the hyperglycæmic action of (I). R. N. C.

**Influence on carbohydrate metabolism of experimentally induced hepatic changes. IV. Blocking of the reticulo-endothelial system with special reference to the Kupffer cell.** T. L. ALTHAUSEN, B. E. BLOMQUIST, and E. F. WHEDON (Amer. J. Digest. Dis. Nutrit., 1935, **2**, 532—540).—Blocking of the reticulo-endothelial cells in rabbits by intravenous injection of C lowered the blood-sugar level, increased the tolerance to ingestion of glucose, decreased mobilisation of glycogen (I) from the liver when adrenaline was injected, and reduced the (I) content of liver and muscle. NUTR. ABS. (*m*)

**Convulsive action of glycerol.** A. LEVI (Boll. Soc. ital. Biol. sperim., 1935, **10**, 780—781). R. N. C.

**Physiological properties of trichloroethylene.** H. TAYLOR (J. Ind. Hyg., 1936, **18**, 175—193).—Continued inhalation of 0·05—0·2% $C_2HCl_3$ by rats and dogs over a period of 6 months caused no pathological condition. H. D.

**Mechanism of the action of citrate ion on the heart and smooth muscle of amphibia.** G. RUSSO (Boll. Soc. ital. Biol. sperim., 1935, **10**, 798—801).—The action is partly a sp. stimulation of the sympathetic nervous system, and partly a non-sp. fixation of $Ca^{\cdot\cdot}$ ions. R. N. C.

**Behaviour of ascorbic acid and glutathione in the organs of guinea-pigs treated with various bacterial poisons. I. Diphtheria toxin. II. Tetanus toxin. III. Koch's tuberculin.** P. NUZZI (Boll. Soc. ital. Biol. sperim., 1935, **10**, 710—714, 714—715, 715—717).—I. Ascorbic acid (I) and glutathione (II) exhibit negligible changes in all the organs.

II. (I) shows no appreciable variation, but (II) is reduced to different extents.

III. (I) falls in the lungs and adrenals. (II) falls very slightly in the same organs and increases in the spleen. R. N. C.

**Action of 2 : 4-dinitrophenol on the isolated heart of the guinea-pig.** M. ALOISI (Boll. Soc. ital. Biol. sperim., 1935, **10**, 746—748). R. N. C.

**Modifications of the physiological action of 3 : 4-dihydroxyphenyl-β-aminobutanol by substitution of methylamino- for the amino-group.** RAYMOND-HAMET (Compt. rend., 1936, **202**, 690—692).—Replacement of the primary by a *sec.*-$NH_2$ increased the hypertensive action of the substance. This effect becomes less marked in lower homologues. A. G. P.

**Pathogenesis of tolylenediamine icterus.** T. OKA (Klin. Woch., 1935, **14**, 861; Chem. Zentr., 1935, ii, 1211).—Effects following injection into dogs are described. H. N. R.

**Diabetogenic activity of substances related to phloridzin.** A. LAMBRECHTS (Compt. rend. Soc. Biol., 1936, **121**, 1364—1366).—Dibromophloridzin and arbutin, but not the azo-dyes azophloridzin, azophloretin, and azophloroglucinol, cause glycosuria when injected into the dog. R. N. C.

**Influence of certain lipins on the growth of a rabbit neoplasm.** A. R. HARNES (J. Lab. Clin. Med., 1935, **20**, 1077—1079).—Subcutaneous injection of maize oil or EtOH-extract of ox brain retards the growth. CH. ABS. (*p*)

**Action of amino-acids on the contractions and the production of lactic acid by the isolated heart.** R. CRISMER (Compt. rend. Soc. Biol., 1936, **121**, 1345—1347).—Lactic acid (I) production is increased by perfusion with neutral solutions containing glycine or phenylalanine; with a solution at $p_H$ 8·5 the increase balances the fall produced by the alkaline medium. The amplitude of contraction $\propto$ (I) production. R. N. C.

**Action of acetylcholine on the formation of lactic acid and decomposition of phosphagen in the isolated muscle of the frog.** D. NACHMANSOHN and A. MARNAY (Compt. rend. Soc. Biol., 1936, **121**, 1311—1314).—The processes are accelerated. The effect of acetylcholine on metabolism persists after the contraction it produces has disappeared, and it is not destroyed by contact for several hr. with the muscle in anaërobiosis. R. N. C.

**Sympathetic regulation of normal blood-sugar and metabolism of tissue-chlorides.** W. LIPSCHITZ (Compt. rend. Soc. Biol., 1936, **121**, 1295—1298).—The increase of blood-sugar and -Cl provoked by adrenaline (I) in rabbits is abolished by ergotamine (II), which causes a fall. Cl is also increased by ligature of an artery, this increase also being abolished by (II). Injection of $CaCl_2$ increases blood-Cl; the increase disappears with that of Ca, but while it persists tissue-NaCl migrates to the blood, probably through sympathetic excitation by Ca in a manner analogous to that of (I) and arterial ligature. R. N. C.

**Action of injectable liver extracts.** H. E. BÜTTNER (Fortschr. Ther., 1935, **11**, 257—264; Chem. Zentr., 1935, ii, 1208). H. N. R.

**Effect of tissue extracts on esterification of cholesterol in serum.** W. M. SPERRY (J. Biol. Chem., 1936, **113**, 599—606; cf. A., 1935, 1536).—When saline extracts of various tissues from different species of animals were incubated with ox, sheep, and human serum, esterification of the free cholesterol occurred, just as when the serum was incubated alone, but in most cases the extracts appeared to inhibit the reaction slightly. The results are not in agreement with those of Shope (A., 1929, 88) and a probable explanation is discussed. Thymol inhibits the esterification in ox serum. J. N. A.

**Reflex and direct respiratory action of some sympathomimetic substances.** E. BECCARI and A. BORIANI (Boll. Soc. ital. Biol. sperim., 1935, **10**, 774—777). R. N. C.

**Pantocaine *L*.** A. A. NABI (Lancet, 1936, **230**, 779—780).—*p*-Butylaminobenzoyldimethylaminoethanol hydrochloride is a satisfactory spinal anæsthetic which produces no marked retention of urine or fall in blood pressure. L. S. T.

**Percaine. I. Action on the isolated frog's heart. II. Action on the isolated rabbit's heart. Comparison with the action of cocaine: antagonism with adrenaline.** R. Santi and B. Zweifel (Boll. Soc. ital. Biol. sperim., 1935, **10**, 648—652, 652—566). R. N. C.

**Anæsthetic action of dialkylbarbituric acids.**—See this vol., 736.

**Action of emetine on the activity of the adrenal and thyroid glands.** R. N. Chopra, J. C. Gupta, and A. C. Roy (Indian J. Med. Res., 1935, **22**, 771—776).—Parallel decreases in thyroid-I and adrenal adrenaline in the rabbit are recorded. R. N. C.

**Amphotropic action of ergotamine (ginergen) on the isolated toad's heart.** G. Russo (Boll. Soc. ital. Biol. sperim., 1935, **10**, 803—805). R. N. C.

**Neutralising action *in vitro* of some chemical substances on the toxicity of curare.** H. Vincent and F. Morel (Compt. rend., 1936, **202**, 803—805).—Very small amounts of the Na salts of oleic, linoleic, ricinoleic, salicylic, di-iodosalicylic, α- and β-hydroxynaphthoic, and methylenebis-β-hydroxynaphthoic acids when added to solutions of curare entirely neutralised the toxicity of the latter as determined by injection in a guinea-pig. J. N. A.

**Invasion of the body by animal poisons.** F. Duran-Reynals (Science, 1936, **83**, 286—287). L. S. T.

**Toxicity and potential dangers of crude "Duprene."** W. F. von Oettingen and W. Deichmann-Gruebler (J. Ind. Hyg., 1936, **18**, 271—272).—The vapour from heated Duprene has no permanent toxic effect. H. D.

**β-Chlorobutadiene (Chloroprene): its toxicity and pathology and the mechanism of its action.** W. F. von Oettingen, W. C. Hueper, W. Deichmann-Gruebler, and F. H. Wiley (J. Ind. Hyg., 1936, **18**, 240—270).—β-Chlorobutadiene is toxic, however administered. H. D.

**Selective adsorption of enzymes by cellulose.** H. Tauber (J. Biol. Chem., 1936, **113**, 753—757).—Cotton adsorbs pepsin (I) and catalase (rabbit's liver) strongly and peroxidase (horseradish) weakly; (I) is eluted by 0·9% aq. NaCl. H. D.

**Formation of respiration enzymes during germination of barley.** H. Fink, H. Haehn, and E. Zenger (Woch. Brau., 1936, **53**, 65—69, 73—77, 83—87, 93—95, 101—103).—The mechanism of respiration is discussed. In a study of the anaërobic phase, the decolorisation of methylene-blue (I) by barley meal (source of dehydrase) is followed (modified Thunberg–Ahlgren technique) in presence of hexose diphosphate (II) ($H_2$ donator), hot aq. extract of yeast (source of co-enzyme), and $PO_4'''$ buffer ($p_H$ 9·0). The dehydrase activity of resting barley is small, but increases markedly during malting (pale); with dark malt, a max. is attained after approx. one half the germination period. The enzyme resists heat-treatment and is not destroyed on kilning, but it is very sensitive to antiseptics and is destroyed by hot EtOH. For given amounts of (I) and (II) there is an optimal concn. of meal; increase in amount of yeast extract causes an acceleration of dehydrogenation up to a definite max. val. A certain min. concn. of (II) is necessary; increases above this cause increased dehydrogenation, but there is no direct proportionality. The time of decolorisation ∝ the concn. of (I) so long as this remains relatively small. Dehydrogenation is optimal at a faintly alkaline $p_H$; with increasing acidity it is inhibited, but the acceleration of decolorisation in strongly alkaline media is due to chemical, and not to enzymic, action. Of numerous substances investigated as donator, (II) gave the greatest acceleration; other hexose phosphates have a smaller effect. Dehydrogenase may be extracted from malt readily by aq. $K_2HPO_4$, but with difficulty by $H_2O$. Malt contains some substance capable of acting as $H_2$ donator, but no co-enzyme. The malt embryo contains the bulk of the dehydrogenase; the endosperm contains relatively little, whilst the rootlets and husk are almost inactive. It has not been possible to identify the products of decomp. of (II) produced by dehydrogenase activity. I. A. P.

**Peroxidase.** M. Tamai (J. Biochem. Japan, 1936, **23**, 1—17).—Purified peroxidase is free from ionic Fe. Addition of $Cu^{\cdot\cdot}$ (but not of $Fe^{\cdot\cdot\cdot}$ or $Mn^{\cdot\cdot}$) activates, whilst that of KCN inhibits to an extent dependent on the purity of the prep. The activity of potato-peroxidase is greatly accelerated by storage of the potato tissue in $H_2O$ and $O_2$. The nature of accompanying impurities, which partly inhibit the enzyme but also protect it from the action of KCN. is discussed. F. O. H.

**Cadmium and oxidation enzymes.** A. Zlatarov (Biochem. Z., 1936, **284**, 448—454).—Cd salts have a pronounced peroxidase- and catalase-like action on $H_2O_2$. Low concns. of $CdCl_2$ or $Cd(OAc)_2$ inhibit and high concns. enhance the activity of blood- and liver-catalase whilst all concns. of $Cd(NO_3)_2$ inhibit the former; other Cd salts have a similar action. F. O. H.

**Spectroscopy of purified enzymes. II. Amylase and peroxidase.** R. Itoh (J. Biochem. Japan, 1936, **23**, 125—130).—Spectroscopic and chemical examination of pancreatic amylase at various stages of purification confirms that it is not protein but carbohydrate in nature. Peroxidase appears to be a compound of protein and porphyrin-Fe complex, the activity being due to the latter (cf. A., 1935, 1535). F. O. H.

**Sisto- and eleuto-amylase.** R. Deplanque (Woch. Brau., 1936, **53**, 137—141).—A lecture.

**Action of α-glucosidase on α-methylglucoside and certain di- and tri-saccharides.** K. Myrbäck and S. Myrbäck (Svensk Kem. Tidskr., 1936, **48**, 64—68).—Differences of action of maltases and invertases from different sources on α-glucosidically-linked sugars show that Weidenhagen's theory of carbohydrase specificity is not generally valid. M. H. M. A.

**Liver-asparaginase.** Y. Suzuki (J. Biochem. Japan, 1936, **23**, 57—69).—Enzyme preps. from calf's and rabbit's liver hydrolyse (determined by $NH_3$ liberation) asparagine, glycyl- and anhydroglycylasparagine, pyrrolidonecarboxylamide (cf. Ishiyama, A., 1933, 723), and glucosamine. The data indicate two types of asparaginase with $p_H$ optima of approx. 8·1. F. O. H.

**Cell membrane as a hindrance to the digestion of plant foods.** E. Mangold and H. Jänsch (Sitzungsber. Ges. naturf. Fr. Berl., 1935, Feb., 40—44).—Heupke's claim that enzymes can penetrate cells and digest their contents is questioned. Nutr. Abs. (*m*)

**New type of enzyme in the intestinal tract.** M. Bergmann and J. S. Fruton (Science, 1936, **83**, 306).—The action of erepsin on substances like glycyl-*l*-proline is due to a special enzyme which, unlike dipeptidase and aminopeptidase, is not appreciably inhibited by $CN'$. As > one quarter of the peptide linkings in proteins such as collagen and gelatin require the action of the new enzyme, its presence in the intestinal mucosa is significant. L. S. T.

**Enzymic histochemistry. XVI. Digestion of keratin by larvæ of the clothes moth (*Tineola bisselliella*, Humm.).** K. Linderstrøm-Lang and F. Duspiva (Compt. rend. Trav. Lab. Carlsberg, 1936, **21**, No. 4, 53—83).—Both the intestinal fluid and a glycerol extract of the intestines of *Tineola* have high proteolytic activity; with casein as substrate the optimum $p_H$ is 9·3. This proteinase has no action on keratin (I) at this $p_H$, nor at the $p_H$ of the intestinal fluid (9·6—10·2). Dissolution of wool, with cleavage of peptide linkings, takes place if a reducing agent (thioglycollic acid) is present to reduce the autoxidised cystine (II). There exists, in the middle intestine, a reducing system, possibly enzymic, able to reduce (II) to cysteine. (I) can thus be digested by the simultaneous action of this reducing system and the proteinase. E. A. H. R.

**Proteolytic action of pancreatic juice, and of trypsin followed by erepsin.** C. Lauresco (Arch. internat. Physiol., 1935, **42**, 169—182).—Successive action of pancreatic juice and erepsin (I) produced a degradation of protein only slightly < that produced by pepsin, trypsin, and (I). This explains why N absorption remains very near to normal even in the absence of the stomach. The resistance offered by gelatin and gliadin may be due to the fact that peptides containing proline or glutamic acid tend to resist splitting by pancreatic juice. Nutr. Abs. (*m*)

**Liberation of ammonia during enzymic proteolysis.** E. F. Terroine and C. Lauresco (Arch. internat. Physiol., 1935, **42**, 205—222).—Proteolysis by pancreatic juice, activated by enterokinase or Ca, is always accompanied by production of $NH_3$. This is least in the first 24 hr. and cannot be explained by processes other than bacterial, although it appears to be modified somewhat by the nature of the proteolytic enzyme used. Nutr. Abs. (*m*)

**Hydrolysis of crystalline pepsin by trypsin.** P. S. Yang (Chinese J. Physiol., 1936, **10**, 1—5).—Trypsin hydrolysed pepsin (I) at $p_H$ 5·6 and 37—39°. The decrease of activity of (I) is accompanied by an increase of $NH_2$-N. J. N. A.

**Proteases and ontogenesis. I. Cathepsin in the chick embryo.** E. Mystkowski (Biochem. J., 1936, **30**, 765—769).—With gelatin, ovalbumin, and lecithovitellin (I) as substrates, the activity of cathepsin in connexion with the embryonic synthesis of protein is very small, with or without cysteine as activator. The optimum $p_H$ is 4·7, whilst with (I) as substrate it is 5·8. The activity is not significantly changed during the whole developmental period of the embryo. The yolk-sac is 15—20 times more active than the embryo. No positive results on synthesis *in vitro* were obtained. J. N. A.

**Phosphatase of the prostate gland. II.** W. Kutscher and A. Wörner (Z. physiol. Chem., 1936, **239**, 109—126; cf. this vol., 111).—The phosphatase is stable at $p_H$ 3·7—6·0, the inactivation at other reactions being independent of the concn. of substrate. Hydrolysis of β-glycerophosphate (I) is optimal at $p_H$ 5·2—6·2 and of phenylphosphoric acid at 4·0—5·4, the optimal concn. of (I) being about 0·153$M$. When the amount of P liberated is about 9%; the extent of hydrolysis ∝ enzyme concn. The rate of reaction decreases with time. The enzyme is not activated by $Mg^{\cdot\cdot}$ and is inactivated by NaF (0·002—0·01$M$), org. solvents, and Et urethane but not by cysteine. Purification by electro-dialysis affords a product (N 7%) liberating 75% of its wt. of $H_3PO_4$ per sec. W. McC.

**Variations in phosphatase activity of bone, kidney, and blood in experimental rickets.** G. Scoz (Boll. Soc. ital. Biol. sperim., 1935, **10**, 823—826).—The bone-Ca and rate of growth of the bones in rachitic rats are < those in normal animals; during curative treatment the rate of growth begins to increase before Ca. Phosphatase (I) in the blood of rachitic animals is increased, whilst kidney- and bone-(I) are increased in winter but diminished in summer. During curative treatment blood-(I) falls whilst kidney- and bone-(I) rise; when the cure is almost complete, bone-(I) is still slightly high whilst blood-(I) is low, as occurs when the ossification process is increased by thyroxine. R. N. C.

**Influence of certain dyes on fermentation and respiration of yeast extract.** L. Michaelis and C. V. Smythe (J. Biol. Chem., 1936, **113**, 717—734).—The effect of a no. of reversibly oxidisable and reducible dyes on the alcoholic fermentation by yeast extract is studied. The dyes fall into 3 groups, viz., (*a*) those that increase the $O_2$ consumption but do not inhibit fermentation, (*b*) those that inhibit aërobic fermentation [the inhibition being suppressed by addition of hexose diphosphate (I)] and are sp. poisons for the enzymes responsible for the synthesis of (I), and (*c*) those that produce an irreversible inhibition of aërobic fermentation due to enzyme (*e.g.*, carboxylase) destruction. No correlation between inhibition and oxidation–reduction potential was obtained. H. D.

**Trehalose in pressed yeast.** K. Myrbäck (Svensk Kem. Tidskr., 1936, **48**, 55—61).—Pressed yeast contains as fermentable carbohydrate 13·3% of glycogen, the remainder being trehalose (I), which is absent from ordinary live yeast and brewer's bottom yeast. It is isolated by extraction of the yeast with aq. EtOH, pptn. of protein, and evaporation (90% yield). The (I) content of pressed yeast falls slowly at 5°, rapidly in air at room temp., but may be preserved by vac. drying. (I) is fermented directly without preliminary conversion into glucose.

M. H. M. A.

**Application of micro-Kjeldahl–Pregl method to determination of total nitrogen in yeast.** M. Sobotka (Mikrochem., 1936, **19**, 81—88).—N is completely converted into $NH_3$ by a short heating with $H_2SO_4$, the oxidation being completed with 30% $H_2O_2$. $Hg(OAc)_2$ is the most suitable catalyst.

J. S. A.

**Occurrence of growth-promoting factor *B* in animal organs.** V. Hartelius and S. Hjorth-Hansen (Compt. rend. Trav. Lab. Carlsberg, 1936, **21**, No. 11, 221—229).—Calf liver contains large amounts of the growth-promoting factor *B* (I) which acts on *Aspergillus niger* and yeast. The (I) content of calf liver is about 5 times that of cod liver, veal, or salted herring; that of cod meat is still lower. Calf- and cod-bile have a weak effect on the growth of yeast and none on that of *A. niger*. The high (I) content of calf liver may be due to the glycogen it contains.

E. A. H. R.

**Effect of acetate on the consumption of succinic acid by moulds.** V. S. Butkevitsch and L. K. Osnickaja (Compt. rend. Acad. Sci., U.R.S.S., 1935, **4**, 345—348).—The consumption of Na succinate (I) by *Aspergillus niger* is greatly restricted by addition of NaOAc, which is itself consumed. Added sugar does not affect the process. Citric acid is produced only if sugar is added. $H_2C_2O_4$ is produced in amounts equiv. to the base liberated by consumption of (I) and NaOAc. The source of succinic acid which sometimes accumulates in moulds may be substances other than sugar and AcOH.

W. McC.

**Palitantin, a metabolic product of *Penicillium palitans*.**—See this vol., 729.

**Staining technique for protozoa.** D. L. Sargent (Stain Tech., 1936, **11**, 49—52).—A modification of Donaldson's I–eosin stain for intestinal protozoa contains colloidal I and aniline-red in dil. solution.

W. O. K.

**Chemistry and physiology of the sulphur bacteria.** H. J. Bunker (Dept. Sci. Ind. Res., Chem. Res., Spec. Rept. No. 3, 1936, 48 pp.).—A review.

**Production of free sulphur from *l*-cystine by a soil bacterium.** H. H. Barber and R. B. Burrows (Biochem. J., 1936, **30**, 599—603).—*Achromobacter cystinovorum*, a new Gram-negative bacillus isolated from soil, decomposes cystine in a medium containing no other source of C, N, or S with formation of $NH_3$, free S, and $CO_2$ in equiv. proportions.

W. O. K.

**Bacterial reduction of sulphates.** J. W. Young (Canad. J. Res., 1936, **14**, B, 49—54).—Anaërobic sulphate-reducing strains of Gram-negative vibrios are isolated from deep well $H_2O$, from soil, and from sewage. They grow best at $p_H$ 5—9 and utilise lactates but not formates as a source of C.

J. L. D.

**Microchemistry of sulphur bacteria.** A. Monti (Boll. Soc. ital. Biol. sperim., 1935, **10**, 690—691).—The endocellular S droplets in colonies of S bacteria are converted into $Ag_2S$ by $AgNO_3$. $Pb(OAc)_2$ removes the droplets in neutral solution, but in conc. KOH the S is partly converted into PbS. $HgCl_2$ and $H_2PtCl_6$ have relatively little action, whilst $OsO_4$ fixes the protoplasm and droplets but does not penetrate the colony.

R. N. C.

**Activity of non-pathogenic bacteria in the thermal waters of Aix-les-Bains and Aix-Burtscheid.**—See this vol., 698.

**Biochemical activities of the acetic acid bacteria.** K. R. Butlin (Dept. Sci. Ind. Res., Chem. Res., Spec. Rept. No. 2, 47 pp.).—A survey.

**Fermentation of mannitol provoked by *B. coli* and *B. lactis aërogenes*.** V. Cianci (Boll. Soc. ital. Biol. sperim., 1935, **10**, 730—732). R. N. C.

**Action of photo-catalysts on the fermentation of lactose determined by *B. coli*.** G. Guerrini (Boll. Soc. ital. Biol. sperim., 1935, **10**, 847—849).—The action of photo-catalysts is stimulant or inhibitory according to the quantity and quality of the catalyst.

R. N. C.

**Catalase activity of lactic acid bacteria.** D. Talce-Niedia (Le Lait, 1936, **16**, 225—232).—Certain strains of *Streptococcus lactis* produce catalase (I), but on culturing they show a low (I) activity (index by the volumetric method of 0·5—1·0). This activity, however, cannot be used as a basis for assessing the qualities of cultures of lactic acid bacteria.

W. L. D.

**Biochemistry of micro-organisms. VII. *Bacterium linens*.** W. Grimmer and J. Schmid (Milch. Forsch., 1936, **17**, 286—302).—*B. linens* liberates leucine, *iso*leucine, and tyrosine from casein and deaminates other $NH_2$-acids. No indole or skatole is formed. The organism is closely related to *B. mesentericus*.

W. L. D.

**Effect of sulphur compounds on fermentation by propionic bacteria.** P. Chaix and C. Fromageot (Compt. rend., 1936, **202**, 983—984).—0·1 mg. of cystine per 5 c.c. is sufficient to stimulate the max. activity of the bacteria. Methionine, glutathione (oxidised or reduced), thiolactic and thioglycollic acid have a similar action.

P. G. M.

**Fixation of nitrogen in leguminous root nodules.** A. I. Virtanen and T. Laine (Suomen Kem., 1936, 9, **B**, 12; cf. A., 1935, 1551).—Nitrites detected in aq. extracts of sand cultures of peas arise from oximes originally present in the cultures. Aspartic acid, formed from $CO_2H{\cdot}CH_2{\cdot}C(N{\cdot}OH){\cdot}CO_2H$, may be the primary product of N fixation.

R. S.

***dl*-Tolylalanine and its bacterial decomposition.**—See this vol., 721.

**Biological oxidations. VI. Oxidation of pyruvic acid by gonococci.** E. S. G. Barron (J. Biol. Chem., 1936, **113**, 695—715; cf. A., 1935, 121).—The oxidation of $AcCO_2H$ by the ketonoxidase from gonococci has a temp. coeff. of 2·87 and is inhibited by $Na_4P_2O_7$, KCN, NaF, and a no. of org. compounds, but not by $H_2S$ and CO. The existence of an activating enzyme for $AcCO_2H$ oxidation is demonstrated.

H. D.

**Antigenic structure of *Vibrio choleræ*. VIII. Specific carbohydrate content and serology of the acid-soluble fractions.** R. W. Linton, B. N. Mitra, and S. C. Seal. **IX. Dissociation and changes in chemical structure.** R. W. Linton, D. L. Shrivastava, and B. N. Mitra (Indian J. Med. Res., 1935, 22, 617—632, 633—657).—VIII. Reducing substances (I) are high in the *A* and *B* acid-sol. fractions of *V. choleræ* but low in the residue. The two fractions probably represent the outer part of the organism. *A* contains most of the serological activity. The distribution of (I) between *A* and *B* shows a parallelism with the smoothness of the organisms, (I) in *A* being $>$ in *B* in smooth organisms. The same parallelism is not shown with agglutinability. (I) are probably derived from the sp. polysaccharide (II) by hydrolysis.

IX. Dissociation in the vibrios is caused by change of (II) content, the appearance of new types of protein and carbohydrates in the organism, or by the presence of two types of (II) in unstable equilibrium in the strain. A third type of (II), containing glucose without aldobionic acid, is present in dissociants of the "medusa-head" type; dissociation to this stage is accompanied by transformation of (II) into a different type without loss. The El Tor vibrios form a chemically distinct group, which is related to the cholera vibrios through (II) and to the $H_2O$ vibrios through (I).

R. N. C.

**Vibrio filtrates.** R. W. Linton, H. Singh, and S. C. Seal (Indian J. Med. Res., 1935, 22, 659—674).—The factors producing the Shwartzmann phenomenon in filtrates from 20-hr. cultures of the four vibrios concerned are not sp., and are conc. by pptn. with EtOH or saturation with $(NH_4)_2SO_4$. Inorg. substances are removed from broth filtrates by fractional pptn. with EtOH, the active material appearing in the second fraction, but the differentiation does not occur with peptone–$H_2O$ filtrates.

R. N. C.

**Action of the sulphonamide radical on experimental streptococcal infection in the mouse.** P. Goissedet, R. Despois, P. Gaillot, and R. Mayer (Compt. rend. Soc. Biol., 1936, 121, 1082—1084).—Aromatic sulphonamides exhibit antistreptococcal activity.

R. N. C.

**Immunological specificity of staphylococci. I. Occurrence of serological types.** L. A. Julianelle and C. W. Wieghard. **II. Chemical nature of the soluble specific substances.** C. W. Wieghard and L. A. Julianelle. **III. Interrelationships of cell constituents.** L. A. Julianelle and C. W. Wieghard (J. Exp. Med., 1935, 62, 11—21).—I. At least two types of sol. sp. substances are derived from staphylococci.

II. Characteristics of two carbohydrates are given. Type *A* is unidentified. Type *B* yields glucose on hydrolysis. Immunological specificity of both types is lost on hydrolysis.

III. The two carbohydrates are type-sp. The protein of staphylococcus is species-sp.

Ch. Abs. (*p*)

**Bactericidal action of some euflavine preparations on *Staphylococcus aureus* and *Bacillus pyocyaneus*.** K. A. Kjær (Dansk Tidsskr. Farm., 1936, 10, 102—104).—Potency of the preps. is only slightly affected by variations in diaminoacridine hydrochloride content of 0·6—85·6%.

M. H. M. A.

**Lipins of tubercle bacilli. XLIII. Composition of leprosin.** R. J. Anderson, J. A. Crowder, M. S. Newman, and F. H. Stodola (J. Biol. Chem., 1936, 113, 637—647).—The neutral wax-like substance [now termed leprosin (I)] previously isolated (A., 1932, 307) from *B. lepræ* is purified by repeated pptn. from $Et_2O$ with $COMe_2$; it has m.p. 50—51°, $[\alpha]_D$ +4° in $CHCl_3$, I val. (Hanus) 5, and is sterol-free. Hydrolysis (EtOH–KOH) gives glycerol, *d*-β-eicosanol (cf. this vol., 311), (probably) *d*-β-octadecanol, myristic, palmitic, stearic, tetracosanoic, and a OH-acid (*leprosinic acid*) [20% of (I)], m.p. 62—63°, $[\alpha]_D$ +4° in $CHCl_3$ (*Me* ester, m.p. 51—52°; *Ac*, m.p. 42—43°, and *Br*-, m.p. 54—55°, derivatives).

H. B.

**"Acid wax" of human tubercle bacilli.** F. Ulzer and H. Gruber (Wiss. Mitt. österreich. Heilsmittelstelle, 1935, 13, 1—3; Chem. Zentr., 1935, ii, 1196).—The unsaponifiability of the "acid wax" (I) and the non-existence of mycol are confirmed. (I) is the only constituent of the $Et_2O$-sol. fraction of the unsaponifiable lipins of tubercle bacilli.

R. N. C.

**Effect of fatty acids on tubercle and other acid-fast bacilli.** S. Iijima (Tôhoku J. Exp. Med., 1935, 25, 424—436).—The inhibitory effect of acids decreases in the order $HCO_2H$, $EtCO_2H$, AcOH, $PrCO_2H$, and progressively to decoic acid, which completely inhibits growth at concn. of 1 in 10,000. Myristic, palmitic, and stearic acids have no action. Na salts are 0·1—0·02 as active as the free acids.

Ch. Abs. (*p*)

***X*-Ray studies of crystallite orientation in cellulose fibres. II.**—See this vol., 670.

**Physico-chemical properties of hog cholera virus. I. Filterability as affected by hydrogen-ion concentration. II. Migration when subjected to electrophoresis. III. Attenuation of virus and production of immunity to hog cholera.** L. H. Schwarte (Iowa State Coll. J. Sci., 1934, 9, 187—193).—I. The virus over a $p_H$ range of 5·0—9·0 passed all filters.

II. The virus migrated to the positive electrode.

III. Attenuation by ageing or by treatment with $CH_2O$ or PhOH, or prep. in dil. blood and saturation with $N_2$, $Cl_2$, $SO_2$, or $CO_2$ did not confer immunity. The latter was attained by saturating dil. blood with $H_2$ or $O_2$.

Ch. Abs. (*p*)

**Isoelectric precipitation of the tobacco mosaic virus complex.** R. J. Best (Austral. J. Exp. Biol., 1936, 14, 1—13).—The virus is reversibly pptd. from the juice at $p_H$ 3—4 (max. $>$ 99% at 3·4). The ppt., which contains 14% of N, consists entirely of virus or of virus united to material from which it cannot be separated by elution, although relatively stable colloidal solutions are obtained by washing with buffer solutions at $p_H$ 2·8—2·3 and 4·5—7·5. W. McC.

**Hormonal properties of the pineal gland.** P. Engel (Wien. klin. Woch., 1935, **48**, 481—486).—A review. R. N. C.

**Effect of adrenal preparations and vitamin-*C* on the sex cycle in castrated mice.** I. Kawakami (J. Pharm. Soc. Japan, 1935, **55**, 599—612).—Neither material produced any effect. Ch. Abs. (*p*)

**Action of various hormones *in vitro* on the normal bone-marrow and in presence of germs. I. Adrenal hormones.** S. Fiorentini (Boll. Soc. ital. Biol. sperim., 1935, **10**, 740—742). R. N. C.

**Effects of stimulation of the adrenal gland on its content of ascorbic acid, adrenaline, and glutathione.** C. C. Kuchel and M. L. Mitchell (Austral. J. Exp. Biol., 1936, **14**, 51—55).—Stimulation results in decrease in the ascorbic acid (I) content, the decrease having no const. relation to the accompanying decrease in adrenaline content. The ratio glutathione : (I) in the whole gland is only slightly affected by stimulation. W. McC.

**Adrenal gland extract causing luteinisation of the ovaries and endometrial hyperplasia.** R. Allen and G. Bourne (Austral. J. Exp. Biol., 1936, **14**, 45—50).—The extract is made with 8% aq. $CCl_3\cdot CO_2H$. The active principle, which is very stable and insol. in $Et_2O$, is not identical with cortin. W. McC.

**Effect of the adrenal glands on calcium metabolism.** I. Schour and J. M. Rogoff (Science, 1936, **83**, 267—268).—Characteristic disturbances in calcification of dentine occurring in the incisors of bilaterally adrenalectomised rats are described. A functional interrelationship between the adrenal and parathyroid glands is again (cf. A., 1934, 1409) indicated. L. S. T.

**Different reactions of the bulbar centre to adrenaline and pituitrin.** U. Sacchi (Boll. Soc. ital. Biol. sperim., 1935, **10**, 671—675). R. N. C.

**Interrelationships among urinary, pituitary, and placental gonadotropic factors.** J. B. Collip (J. Amer. Med. Assoc., 1935, **104**, 556—558).—A review. Ch. Abs. (*p*)

**Pituitary gonadotropic hormones.** P. E. Smith (J. Amer. Med. Assoc., 1935, **104**, 553—556).—A review. Ch. Abs. (*p*)

**General physiology of the anterior pituitary.** P. E. Smith (J. Amer. Med. Assoc., 1935, **104**, 548—553).—A review. Ch. Abs. (*p*)

**Purified growth-hormone from ox anterior pituitary.** E. Dingemanse and J. Freud (Acta Brev. neerl. Physiol., 1935, **5**, 39—40).—The pituitary is dried with excess of $COMe_2$ at low temp. and extracted with alkali. The hormone is purified by repeated adsorption on norite, elution with PhOH, and pptn. with $EtOH–Et_2O$ (1 : 2). It is free from thyrotropic and lactogenic hormones, and is stable for 3 weeks over $P_2O_5$. R. N. C.

**Effect of anterior pituitary hormones on the male eel.** B. Schreiber (Boll. Soc. ital. Biol. sperim., 1935, **10**, 818—821). R. N. C.

**Malignant tumours of the female genital organs as sources of hormones.** H. Siebke (Z. ges. Naturwiss., 1935, **1**, 70—71; Chem. Zentr., 1935, ii, 1197).—Anterior pituitary hormones are found in the urine of women at the climacteric and menopause, or after irradiation of the genital organs or castration. Sex hormones appear in the urine of women with carcinoma of the genital organs or columnar cell carcinoma but disappear with the appearance of cachexia. R. N. C.

**Tumour of the pituitary induced with follicular hormone.** B. Zondek (Lancet, 1936, **230**, 776—778; cf. this vol., 389). L. S. T.

**Physiology of œstrogenic principles.** E. Allen (J. Amer. Med. Assoc., 1935, **104**, 1498—1502).—A review. Ch. Abs. (*p*)

**Effects of prolonged administration of œstrin in rats.** C. S. McEuen, H. Selye, and J. B. Collip (Lancet, 1936, **230**, 775—776). L. S. T.

**Isolation of œstrone and equilin from pregnant mare's urine.** D. Beall [with M. Edson] (Biochem. J., 1936, **30**, 577—581).—The acid-hydrolysed urine is extracted with PhMe, the "weak phenols" are separated by extraction with solvents, and after vac. distillation divided into $C_6H_6$-sol. and -insol. fractions. The ketonic compounds in the former are pptd. by $Hg(OH)_2–NH_3$, the equilin (I) and œstrone (II) in this ppt. being separated by EtOH. Acid hydrolysis of the equilin complex dissolved in the EtOH, followed by removal of the EtOH and vac. distillation, yielded a crude distillate from which pure (I) was recrystallised from 80% EtOH. Similarly, the Hg–ketone complex yielded a residue from which crude (II) is obtained by sublimation, purification by the quinoline reaction, and crystallisation from EtOH. (II) is directly isolated from the $C_6H_6$-insol. fraction by the quinoline reaction and recrystallisation. W. O. K.

**17-Ethyltestosterone. $\Delta^5$-Pregnene-3 : 20-dione.**—See this vol., 727.

**Culture *in vitro* of the female genital apparatus with folliculin.** F. Guercio and R. Arnone (Boll. Soc. ital. Biol. sperim., 1935, **10**, 622—624). R. N. C.

**Isolated amœboid cells observed in cultures *in vitro* of uterine tissue (mucosa and muscular fibres) of the adult rabbit treated with gonadotropic hormone and folliculin.** F. Guercio (Boll. Soc. ital. Biol. sperim., 1935, **10**, 624—626). R. N. C.

**Action of folliculin and testicular extract on the residual chromic index.** M. Polonovski, H. Warembourg, and J. Driessens (Compt. rend. Soc. Biol., 1936, **121**, 1451—1452).—Folliculin raises the index whilst testicular extract depresses it; the rise or fall in cancerous blood is > in normal blood. R. N. C.

**Œstrogenic action of androsterone.** E. Wolff and A. Ginglinger (Compt. rend. Soc. Biol., 1936, **121**, 1476—1478). R. N. C.

**Double (masculinising and feminising) action of androsterone on the genital tract of the chick embryo.** E. Wolff (Compt. rend. Soc. Biol., 1936, **121**, 1474—1476). R. N. C.

**Male hormones and accessory substances.** R. Deanesly and A. S. Parkes (Lancet, 1936, **230**, 837—839).—In rats, the activity of androsterone or testosterone is markedly increased by an increase in the amount of various media, *e.g.*, olive, arachis, or castor oil, and $OH\cdot CHMe\cdot CH_2\cdot OH$, and by the addition of palmitic acid to the oil solution of testosterone. L. S. T.

**Biological properties of testosterone.** V. Korenchevsky (Nature, 1936, **137**, 494).—The effects of testosterone (I) on castrated male rats and on ovariectomised rats are described. Like androsterone and androsteronediol, (I) has some of the important properties of female hormones. L. S. T.

**Preparation of vagotonin free from insulin.** D. Santenoise, T. Brieu, and E. Stankoff (Compt. rend. Soc. Biol., 1936, **121**, 1420—1422).—Depressor-free pancreatic extract is dissolved in $H_2O$ and the vagotonin (I) is repeatedly pptd. with LiCl at $p_H$ 2·75 to remove impurities, dissolved in EtOH, and pptd. with $Et_2O$ at —10°. Insulin is removed by pptn. with 0·2% $K_4Fe(CN)_6$ at $p_H$ 3·2, and (I) is then repeatedly pptd. at $p_H$ 2·5 with LiCl and dissolved in $H_2O$, the $p_H$ is adjusted to 6·0 with LiOH, and LiCl and $K_4Fe(CN)_6$ are removed by dialysis; (I) is then repeatedly pptd. with EtOH and $Et_2O$, washed, and dried over $P_2O_5$. R. N. C.

**Effect of previous diet and insulin administration on adrenaline hyperglycæmia.** R. Boller and K. Makrycostas (Klin. Woch., 1935, **14**, 646—647).—Hyperglycæmia due to adrenaline (I) is not affected by regulated diet for 6 days before injection. Administration of daily increasing doses of insulin up to the tolerance limit increases the response to (I); (I) secretion is also increased. R. N. C.

**Action of insulin on the ovarian cycle.** A. Crainiceanu and L. Copelman (Compt. rend. Soc. Biol., 1936, **121**, 1303—1304). R. N. C.

**Blood-sugar, -chlorine, and -protein curves after injection of insulin.** G. dell' Acqua (Boll. Soc. ital. Biol. sperim., 1935, **10**, 761—765).—Following injection of insulin into normal and diabetic subjects, the hyperchloræmia $\propto$ the hypoglycæmia, both levels showing small fluctuations; blood-proteins vary irregularly. R. N. C.

**Insulin and body-weight. I. Variations in body-weight, glycogen content, and iodine value of adipose tissue.** E. Boeri, G. Scoz, and P. Baer. **II. Variations of the composition of adipose tissue in insulinised animals.** P. Baer, G. Scoz, and E. Boeri (Boll. Soc. ital. Biol. sperim., 1935, **10**, 680—682, 682—685).—I. Glycogen and the I val. of the adipose tissue of rats and dogs are increased if > 6 daily injections of insulin (I) are given.

II. The $H_2O$ content of the adipose tissue increases during the first 5—10 days of treatment, whilst fat decreases. Later, $H_2O$ falls, and fat, glycogen, the I val., and body-wt. increase for 10 days, the body-wt. subsequently remaining const. whilst the other vals. tend to return to normal. With carbohydrate (II) nutrition, (I) tends to induce synthesis of fats from (II). R. N. C.

**Effect of thyroxine on the protein-sulphur of the liver in the guinea-pig.** G. Scoz, P. L. Micheli, and T. Gualtierotti (Boll. Soc. ital. Biol. sperim., 1935, **10**, 829—830).—S falls sharply in the first few days, afterwards rising steadily. R. N. C.

**Effect of thyroxine on the extractable sulphur and vitamin-*C* content of the liver of the guinea-pig.** G. Scoz and T. Gualtierotti (Boll. Soc. ital. Biol. sperim., 1935, **10**, 830—832).—Extractable S of liver varies inversely and vitamin-*C* directly with body-wt. R. N. C.

**Effect of thyroxine on the phosphatasic power of the liver in the guinea-pig.** G. Scoz and G. Cantoni (Boll. Soc. ital. Biol. sperim., 1935, **10**, 833—834).—The phosphatasic power falls and rises again with the wt. of the liver. R. N. C.

**Effect of thyroxine on the catheptic and amylolytic activities of the liver in the guinea-pig.** G. Scoz and L. de Caro (Boll. Soc. ital. Biol. sperim., 1935, **10**, 826—828).—The activities are increased proportionately during the first few days when body-wt. falls; in the succeeding period the amylase activity falls below normal. R. N. C.

**Action of thyroxine on body-weight and the weight and nitrogen content of some internal organs of the rat.** G. Scoz and P. L. Micheli (Boll. Soc. ital. Biol. sperim., 1935, **10**, 687—689).—Thyroxine increases the wt. of the liver and kidney of the rat, but the N contents of the dry organs are unaffected. R. N. C.

**Thyrotropic hormone in non-pituitary tissues.** L. Ballif and I. Ghersovici (Compt. rend. Soc. Biol., 1936, **121**, 1437—1438).—The hormone is not present in the ovary. R. N. C.

**Induction of mammary ducts.** A. Deakin (Nature, 1936, **137**, 619—620).—Evidence for the presence of an inducing substance, sp. for a particular group of animals, which is responsible for the development of mammary ducts, is discussed. L. S. T.

**Lactation and pregnancy.** P. de Fremery and P. J. Denekamp (Acta Brev. neerl. Physiol., 1935, **5**, 44—46).—Prolactin causes lactation and abortion in pregnant animals. R. N. C.

**Incidence of rickets. "Gallosterol" as a source of vitamin-*A* with normal dietary phosphorus and calcium.** S. Murao (J. Biochem. Japan, 1936, **23**, 71—90).—Deoxycholic acid (I) has a growth-inhibitory action on normal rats and, to a greater extent, on rats on vitamin-*A*- and -*D*-free diet; the effect does not occur in rats with excessive feeding of irradiated ergosterol (II). Administration of (II) irradiated for varying periods to rats on -*A*- and -*D*-free diets produces corresponding differences in the period necessary for onset of *A*-avitaminosis. The effect of (I)-vitamin-*A* ("gallosterol") on the incidence and degree of avitaminosis is described. F. O. H.

**Effect of solvents on the spectral curve of vitamin-*A* and on its photochemical degradation.** A. Chevallier, P. Dubouloz, and S. Manuel

(Compt. rend. Soc. Biol., 1936, **121**, 1495—1498).—The absorption curve shows slight modifications in different solvents, the max. in $C_6H_{14}$ being shifted somewhat to the right of that in EtOH. Vitamin-*A* in $C_6H_{14}$ solution is degraded photochemically to a series of products, the absorption max. of which lie progressively further to the right of that of -*A*. R. N. C.

**Values of the motor chronaxia of the normal guinea-pig and the hepatic vitamin-*A* content.** A. Chevallier and L. Espy (Compt. rend. Soc. Biol., 1936, **121**, 820—822).—Chronaxia and hepatic vitamin-*A* are related. R. N. C.

**Localisation of vitamin-*A* in red blood corpuscles during their evolution in vertebrates.** P. Joyet-Lavergne (Compt. rend., 1936, **202**, 1101—1102; cf. this vol., 257).—The content and localisation of the vitamin (I) in the corpuscles depends on their stage of evolution. The (I) content of young corpuscles is $>$ that of old. When the corpuscles have a nucleolus (I) is localised there. In young corpuscles (I) is sometimes diffused throughout the nucleus. W. McC.

**Content of vitamin-*A* in the liver of fœtus and new-born.** W. Neuweiler (Z. Vitaminforsch., 1936, **5**, 104—110).—The % content of vitamin-*A* in the liver of fœtal and new-born man is approx. equal to that in the liver of adults. F. O. H.

**Vitamin-*A* value of halibut-liver oil.** B. Ahmad (Indian Med. Gaz., 1935, **70**, 70—71).—Samples of oil failing to produce improvement in general health of children contained 25 times as much vitamin-*A* as did standard cod-liver oil, and cured xerophthalmia in -*A*-deficient rats. Ch. Abs. (*p*)

**Standardisation and determination of vitamin-*A*.** E. M. Hume and H. Chick (Med. Res. Counc. Spec. Rep. Ser. No. 202, 1935, 61 pp.).—The specimen of carotene first used as a provisional international standard in 1931 was only 60% pure. It is recommended that 0·0006 mg. of pure β-carotene (I) should now be adopted as the international unit. The maintenance of the yellow colour of (I) is a trustworthy indication of the preservation of biological activity. Coconut oil with addition of quinol as a stabiliser is recommended as solvent. The potency of oil X, of the U.S.P., now adopted as a subsidiary international standard is 3000 international units per g. For the spectrophotometric determination of vitamin-*A* the factor 1600 is provisionally recommended for converting the extinction coeff. ($E^{1\%}_{1\,\text{cm.}}$ at 328 mμ) into international units of -*A* per g. Nutr. Abs. (*m*)

**Content of (*a*) vitamin-*A*, (*b*) vitamin-*C* in Hunan lachiao, *Capsicum annuum*, L., var. *longum*.** H. C. Hou (Chinese J. Physiol., 1936, **10**, 171—178, 179—185; cf. Szent-Györgyi, A., 1933, 433).—(*a*) Dried lachiao pods are fairly rich in vitamin-*A*, 0·3 g. of the powder giving a growth response in rats similar to that obtained with 0·006 mg. of carotene. Approx. one half is extracted by boiling EtOH.

(*b*) The fresh pods contain -*C*, 0·5—1·0 g. per day protecting guinea-pigs from scurvy. The -*C* content is entirely lost on drying. J. N. A.

**Vitamin-*A* and -*D* content of the liver of newborn infants.** K. U. Toverud and F. Ender (Acta paediat., 1935, **18**, 174—191). **Vitamin-*A* and *D*- in the liver of the newborn.** K. U. Toverud and F. Ender (Norsk. Mag. Laegevidenskapen, 1935, **96**, 947—960).—In 97 cases the vitamin-*A* val. was 0·2—517 blue units per g. of liver (mean 47·6 for premature, 28·8 for full term infants). These variations corresponded with variations in the -*A* content of the maternal diet in pregnancy. As regards -*D* content of livers from 44 of the above cases, 24 showed completely negative results, 15 slight healing of rickets in the test rats, and 5 fair healing, the -*D* content depending on the richness of the maternal diet. Nutr. Abs. (*m*)

**Vitamin-*A* and -*B* requirements of young rats at a particular period of growth and when given a high-carbohydrate diet.** L. Randoin and R. Netter (Compt. rend., 1936, **202**, 1105—1107).—Newly weaned rats, on a diet rich in carbohydrate, but deprived of vitamin-*A*, continue to grow normally for about 6 weeks without sumptoms of avitaminosis-*A* if they receive sufficient -*B*. Deprivation of -*B* with or without that of -*A* prevents growth and results in early death. W. McC.

**Vitamin-*B* groups.** A. G. van Veen (Geneesk. Tijds. Nederl.-Indië, 1934, **74**, 1495—1603; Chem. Zentr., 1935, ii, 1203). R. N. C.

**Vitamins and cultures *in vitro*. I. Action of vitamin-*B* on embryonal tissue cultures.** F. Rossi (Boll. Soc. ital. Biol. sperim., 1935, **10**, 843—847).—The vitamin exerts a toxic action, but in small concns. produces an initially increased rate of growth. R. N. C.

**Pharmacological action of vitamin-*B* preparations and their constituents, particularly adenylthiomethylpentose.** C. Hasegawa (Fukuoka Acta med., 1935, **28**, 122—123).—A yeast extract containing *B*-vitamins caused stoppage of the frog's heart and of intestinal movements, with lowering of the blood-pressure, in rabbits. These effects were not produced by cryst. oryzanin, possessing a known -$B_1$ activity, but were produced by autoclaved yeast extract or by a mixture of adenylthiomethylpentose (I), adenine, nicotinic acid, hypoxanthine, and choline in the proportions in which they were present in the extract. The effects were similar to those produced by (I) and were considered to be due to (I). Nutr. Abs. (*m*)

**Dynamics of the symptoms of polyavitaminosis in dogs.** M. S. Levinson (Z. Vitaminforsch., 1936, **5**, 81—104).—Dogs fed on autoclaved diets develop polyavitaminosis within 2½—3 months. During the latent period (2 months), there are no outward symptoms but abnormalities in $H_2O$–NaCl balance, diuresis, excretion of $NH_3$ and urea, and blood elements occur. The onset of ataxia, polyneuritis, skin lesions, etc. during the following period is mainly characteristic of *B*-avitaminosis. F. O. H.

**Control and revision of the international standard for vitamin-*B*.** A. Allegri (Boll. Soc. ital. Biol. sperim., 1935, **10**, 836—839). R. N. C.

**Isoelectric point of vitamin-$B_1$.** G. NARASIMHAMURTHY (Current Sci., 1936, 4, 586—587).—The isoelectric point of pure vitamin-$B_1$ determined by electrophoresis and micro-cataphoresis methods is $p_H$ 9·2. F. N. W.

**Isoelectric point of vitamin-$B_1$.** B. C. GUHA (Current Sci., 1936, 4, 653).—Comments (cf. preceding abstract). F. A. A.

**Potentiometric titrations of vitamin-$B_1$ and thiochrome.** A. G. OGSTON and R. A. PETERS (Biochem. J., 1936, 30, 736—741).—The titration curve of vitamin-$B_1$ on the acid side is completely described by one basic group of $p_K$ 4·8. Thiochrome shows a basic $p_K$ of 5·6 and, like -$B_1$, a tendency for a drifting val. to the alkaline side. It has no -$B_1$ activity by catatorulin test. P. W. C.

**Value of increased supply of vitamin-$B_1$ and iron in the diet of children. II.** J. R. ROSS and P. SUMMERFELDT (Amer. J. Dis. Children, 1935, 49, 1185—1188).—Increases in wt. resulting from substitution of special mixed cereals for ordinary cereals in the diet were > those attributable to their vitamin-*B* content. CH. ABS. (*p*)

**Lactoflavin, a possible contaminant of vitamin-free diets.** G. C. SUPPLEE, G. E. FLANIGAN, Z. M. HANFORD, and S. ANSBACHER (J. Biol. Chem., 1936, 113, 787—792).—Lactoflavin (I), determined by the fluorescence method, is present in crude and certain " vitamin-free " caseinogen (II) preps. Repeated extraction of crude (II) with dil. aq. NaCl at the isoelectric point gives a prep. free from (I). H. D.

**Nature and partial isolation of the substance curative of the pellagra-like condition [in rats and chicks] due to dietary egg-white.** J. G. LEASE (Z. Vitaminforsch., 1936, 5, 110—118).—The principle (I) (not identical with vitamin-$B_2$) is not extracted from liver or kidney (in which it occurs) by org. solvents or $H_2O$. Acid- or protease-hydrolysates, however, yield aq. extracts containing (I), which is pptd. (from MeOH) by $Et_2O$ and EtOAc but not by $COMe_2$ or (from $H_2O$) by protein-precipitants (excepting phosphotungstic acid). (I) is dialysable, gives a positive biuret reaction, and is stable to heat, acids, and alkalis but not to oxidation, autoclaving, or ultraviolet irradiation. (I) is active when administered orally or parenterally. F. O. H.

**Further evidence for the existence of vitamin-$B_4$.** O. L. KLINE, C. A. ELVEHJEM, and E. B. HART (Biochem. J., 1936, 30, 780—784; cf. this vol., 390).—The existence of vitamin-$B_4$ and its necessity for the normal nutrition of rats are confirmed (cf. Reader, A., 1930, 380). J. N. A.

**Treatment of infantile scurvy with ascorbic acid.** E. GOETTSCH (Amer. J. Dis. Children, 1935, 49, 1441—1448).—Intravenous injection of 400 mg. of ascorbic acid caused rapid healing. Calcification was more rapid than when orange juice was given. CH. ABS. (*p*)

**Effect of administration of vitamin-*C* on the reticulocytes in certain infectious diseases.** J. M. FAULKNER (New England J. Med., 1935, 213, 19—20). CH. ABS. (*p*)

**Effect of ascorbic acid on coagulation of blood in normal and pathological conditions.** L. COTTI (Boll. Soc. ital. Biol. sperim., 1935, 10, 697—700).—Ascorbic acid injected intravenously frequently reduces the time of coagulation, particularly in hæmophilia. R. N. C.

**Action of ascorbic acid on blood coagulation *in vitro* and *in vivo* in the rabbit.** C. J. HANUT (Compt. rend. Soc. Biol., 1936, 121, 1338—1340).—Ascorbic acid accelerates coagulation of recalcified oxalated blood *in vitro* at a concn. of 0·005—0·02% and retards it at higher concns. through its effect on the reaction of the mixture; when neutralised it does not affect coagulation. It accelerates coagulation of recalcified oxalated or citrated plasma from rabbits when injected intravenously. R. N. C.

**Action of ascorbic acid on blood coagulation in normal or vitamin-*C*-deficient guinea-pigs.** C. J. HANUT (Compt. rend. Soc. Biol., 1936, 121, 1341—1342).—Ascorbic acid accelerates coagulation in normal animals, but does not affect it in the deficient animal that is showing signs of scurvy. R. N. C.

**Anticoagulant action *in vitro* of complex salts derived from vitamin-*C* and copper, titanium, or zinc, associated with other metals.** F. ARLOING, A. MOREL, and A. JOSSERAND (Compt. rend. Soc. Biol., 1936, 121, 1479—1480).—The anticoagulant actions of Cu and Ti complexes are < those of Fe complexes. Zn in an Fe complex increases its anticoagulant action, unless Pb is also present, whilst complexes containing Zn without any other multivalent metal show the greatest anticoagulant action. R. N. C.

**Modifications of the antirachitic activity of orthophosphoric acid by fixation of alcoholic, phenolic, and glucosidic chains.** R. LECOQ and M. L. BARBAN (Bull. Soc. sci. Hyg. aliment., 1935, 23, 121—132; cf. A., 1935, 109, 238, 657).—The activity of $H_3PO_4$ is not seriously affected by esterification with alcohols; it is slightly retarded in Na alkyl phosphates and accelerated in the Ca salts. Phenolic esterification inhibits the activity. The activity is scarcely affected by esterification with open-chain sugars, whether or not basic groups are present, but is largely inhibited by esterification with inositol. R. N. C.

**Ascorbic acid as a precursor of serum complement.** F. MARSH (Nature, 1936, 137, 618—619).—The complement complex diminishes or even disappears when ascorbic acid (I) is withdrawn from the food of the guinea-pig, and is restored to normal level by a diet rich in (I). L. S. T.

**Action of vitamin-*C* on diphtheria toxin and the sensitivity of the whooping-cough bacillus to quinol and vitamin-*C*.** O. GROOTTEN and N. BEZSSONOFF (Ann. Inst. Pasteur, 1936, 56, 413—426; cf. A., 1935, 1542).—Massive doses of neutralised ascorbic acid increase the resistance of guinea-pigs to diphtheria toxin. The activity is distinctly < that reported by Harde (A., 1934, 1271). H. G. R.

**Capacity of synthesis of ascorbic acid in the fœtus.** A. GIROUD, A. S. RUIZ, R. RATSIMAMANGA, M. RABINOWICZ, and E. HARTMANN (Compt. rend. Soc.

Biol., 1936, **121**, 1062—1063).—Fœtal ascorbic acid (I) is $>$ maternal (I) in the organs of the rabbit, rat, and guinea-pig, but less in cattle and sheep; synthesis is probable in the first three species. R. N. C.

**Diminution of the iodine value of the liver- and adrenal fats of the guinea-pig in avitaminosis-*C*.** L. de Caro and M. Giani (Boll. Soc. ital. Biol. sperim., 1935, **10**, 835). R. N. C.

**Variations of the ascorbic acid content in the puerperal state. I.** F. Guercio, G. Picinelli, and H. Hamburger (Boll. Soc. ital. Biol. sperim., 1935, **10**, 640—643).—Introductory. R. N. C.

**Vitamin-*C* content of the aqueous humour and its antiscorbutic action.** C. Cella and I. D. Georgescu (Compt. rend. Soc. Biol., 1936, **121**, 1116—1119). R. N. C.

**Vitamin-*C* content of different parts of the nervous system.** F. Plaut and M. Bülow (Z. ges. Neurol. Psychiat., 1935, **153**, 182—192).—The ascorbic acid content of all parts of the human brain declined with advancing age but at relatively different rates; the cerebral content was greatest in the fœtus, the cerebellar content in infancy, and that of the spinal cord in old age. The content of the cerebral and cerebellar cortex was $>$ that of the medulla at all ages except in senility. Observations on the rabbit, dog, cat, and calf gave comparable results. Nutr. Abs. (*m*)

**Distribution of vitamin-*C* in different parts of common Indian foodstuffs.** M. N. Rudra (Biochem. J., 1936, **30**, 701—703).—The vitamin-*C* (I) distribution in the skin, flesh, leaves, and seeds of 21 different fruits and vegetables was studied. (I) is more conc. in the skin than in the flesh; with root vegetables the greatest concn. is in the leaves. With animal foods the concns. were in the order: liver$>$kidney$>$bone-marrow$>$milk$>$heart$>$muscle. H. D.

**Determination of ascorbic acid.** K. Wachholder and H. H. Podestà (Z. physiol. Chem., 1936, **239**, 149—161).—The methods of Bezssonoff *et al.* (A., 1934, 1146), Fujita *et al.* (A., 1935, 793), and Tillmans are not sp. and should be rejected. Those of Folin (A., 1930, 630) and Martini *et al.* (A., 1934, 1271) are trustworthy but for each animal, organ, and fluid tests must be made to show which of the two methods gives the lower and hence more sp. val. W. McC.

**Chemical and biological assay of vitamin-*C*.** H. C. Hou (Chinese J. Physiol., 1936, **10**, 191—196).—In guinea-pigs the curve of response to different amounts of ascorbic acid (I) was a straight line. Satien pumelo juice gave nearly the same chemical and biological assay vals. for (I). Green amaranth grown with exclusion of short ultra-violet rays showed a difference between the two vals., but this was $<$ that for amaranth grown in the open. Mixtures containing (I) and small amounts of lucerne were more active than when larger amounts of the latter were used. J. N. A.

**Antirachitic factor in human milk.** I. A. Sabri and M. M. Fikri (Arch. Dis. Childhood, 1935, **10**, 377—380).—Irradiated (ultra-violet) fat from the milk of healthy mothers with normal children afforded nearly complete protection from rickets when incorporated in the rachitogenic ration of rats to the extent of 4%, whilst that from mothers whose children were rachitic gave similar protection only when it constituted 8% of the diet. Nutr. Abs. (*m*)

**Comparison of the vitamin-*D* contents of Guernsey and Shorthorn butter (milk).** S. K. Kon and K. M. Henry (Biochem. J., 1936, **30**, 776—779).—Under similar conditions of feeding and management, butter fat from Guernsey and Shorthorn cows contained 0·35 and 0·28 international units of vitamin-*D* per g., respectively; the difference is not statistically significant. If the relationship is generally valid, the relative contents of the two milks could be expressed by the ratio of the % fat. J. N. A.

**Dietary requirements for lactation. V. Presence of a second lactation factor in yeast.** W. Nakahara, F. Inukai, S. Kato, and S. Ugami (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1936, **29**, 47—52; cf. this vol., 227).—Yeast contains a second dietary factor, $L_2$, necessary for lactation. It is different from $L_1$ (originally called $L$ and obtained from liver and yeast) and is non-adsorbable on acid earth. J. N. A.

**Nutritional deficiency causing gizzard erosions in chicks.** H. J. Almquist and E. L. R. Stokstad (Nature, 1936, **137**, 581—582).—Gizzard erosion is a separate deficiency disease which can be corr. by a new fat-sol. factor, probably vitamin in nature, present in kale and lucerne. The new factor, which is localised in the saponifiable fraction of the extracts, is distinct from the anti-hæmorrhagic vitamin. L. S. T.

**Biological effectiveness of $\alpha$-particles as a function of ion concentration produced in their paths.** R. E. Zirkle (Amer. J. Cancer, 1935, **23**, 558—567).—The effectiveness of irradiation ($B$) of fern spores depends on the no. of ions produced in the nucleus and on the ionisation per unit path ($I$) which varies in a characteristic manner along the path. The relationship, $B=kI^{2\cdot5}$, is established ($k$ is a proportionality const.). Ch. Abs. (*p*)

**Inheritance of sugar content in cucurbits.** V. V. Arasimovitsch (Bull. Appl. Bot. U.S.S.R., 1934, [iii], No. 5, 5—30).—Inheritable characteristics in respect of total sugars, sucrose (I), fructose (II), and glucose (III) are frequently observed in hybrids. (I), (II), and (III) are polymer characters, are dominant for some hybrids and absent from others. Dominance of (III) is more frequent than that of (II). (I) is often polymer-recessive. Ch. Abs. (*p*)

**Distribution and translocation of sugars in sugar-beet. I. Sugars in the tissue elements of sugar-beet in relation to its sugar content. II. Connection between vascular bundles of separate rings in the root and vascular bundles of separate leaves.** E. F. Votchal (Nauch. Zap. Sach. Prom., 1934, **11**, Book 40, No. 2, 34—36, 36—38). Ch. Abs. (*p*)

**Breeding of coumarin-free clover.** R. B. Geltschinskaja and M. A. Bordunova (Bull.

Appl. Bot. U.S.S.R., 1934, [iii], No. 5, 315—323).—The coumarin content of clover varies with individual plants and increases up to the flowering period. Vals. for red clover were 1·0—0·056 and for yellow clover 0·86—0·062%. Ch. Abs. (*p*)

**Chemotropic irritation of roots.** B. Niklewski, M. Kahlówna, and M. Dydówna (Polish Agric. Forest. Ann., 1935, **34**, 457—489).—$K_2HPO_4$, $KH_2PO_4$, $K_2SO_4$, and $KNO_3$, even in 0·0001$M$ solutions, caused irritation of *Sinapis* roots. $NH_4Cl$, KCl, NaCl, and $CaCl_2$ had little or no action. Non-electrolytes from stall manure, humus, etc. were irritant at dilutions of 1 in $10^8$. The action is associated with substances of certain mol. size. Ch. Abs. (*p*)

**Ionic antagonism in the phenomenon of imbibition.** D. Kohler (Compt. rend. Soc. Biol., 1936, **121**, 1308—1311).—$Na^{\cdot}$, $K^{\cdot}$, $Mg^{\cdot\cdot}$, and $Ca^{\cdot\cdot}$ act antagonistically to one another in their effects on imbibition by *Laminaria*, the coeff. of imbibition of mixtures of two of the ions being always < the calc. val. assuming that the effects are additive. $Ca^{\cdot\cdot}$ exhibits the greatest antagonism to the other ions. R. N. C.

**Kinetics of penetration. XIII. Effect of $p_H$ on the entrance of potassium into *Nitella* at low concentrations.** A. G. Jacques (Proc. Nat. Acad. Sci., 1936, **22**, 191—193).—Between $p_H$ 6 and 8, the tendency of K to enter the sap of *Nitella* cells from external solutions in which $[K^{\cdot}]=10^{-5}M$ decreases with rise of $p_H$, the [Cl′] remaining const. F. A. A.

**Moisture relations of pecan leaves.** A. H. Finch and C. W. Van Horn (Science, 1936, **83**, 260).—The % of $H_2O$ in mature leaves is practically const. and independent of differences in soil-$H_2O$ when conditions for max. transpiration obtain. A considerable degree of drought may occur before transpiration ceases or before $CO_2$ entrance into the leaf and the interruption of photosynthesis takes place. With a reduced N content and practically unimpaired photosynthesis conditions favouring carbohydrate storage are produced by moderate drying of the soil. Soil-moisture control may be an important means of regulating the formation and utilisation of carbohydrate reserves in the tree. L. S. T.

**Cell sap of *Characeæ*.** R. Collander (Protoplasma, 1936, **25**, 201—210).—Comparison of plants grown in fresh and in brackish $H_2O$ shows differences in sap concn. which are ≪ those in the two media. The difference between the total salt concn. in the sap and that of the corresponding medium is approx. the same in both cases. The case of absorption of cations is in the order K>Na>Ca, Mg. The ratio K/Na in the sap varies with the species. A. G. P.

**Relationship of the phosphate concentration of solution cultures to the type and size of root systems and the time of maturity of certain plants.** A. L. Sommer (J. Agric. Res., 1936, **52**, 133—148).—Increasing $[PO_4''']$ in the nutrient is associated with a decreasing root/top ratio and later maturation. A. G. P.

**Rôle of potassium in the sugar synthesis of *Sorghum saccharatum* (sugar sorghum).** I. N. G. Chokkanna (Z. Pflanz. Düng., 1936, **43**, 43—69).—In flowing-nutrient cultures K protects the plant to some extent against the ill-effects of low temp. The height of the plants and the stem/leaf (wt.) ratio decrease with increasing K content. With conc. (stationary) media the major portion of the K intake occurs in the early growth stages. Evidence of "luxury" consumption is obtained. With increasing K dosage the ratio N/K and the amounts of Ca and P taken up by the plant decline. The ratio protein-/total N in leaves is > in stems and is unaffected by the K supply. The total sugar and the % sucrose (I) in the total increase with the K given. Within the plant K tends to maintain a neutral sap and suppress the inversion of (I) by acids or enzymes. A. G. P.

**Effect of glycerol and mannose on metabolism of the nucleus in [embryonic cells of] the lupin.** G. Deloffre (Compt. rend. Soc. Biol., 1936, **121**, 1100—1103).—Glycerol (I) and mannose (II) are both assimilable, producing regeneration and preventing diminution of the nucleus. (I) is more assimilable than (II), but < glucose. (II) acts partly as an assimilable substance, and partly as a toxic substance, causing withering and decay of the embryo. R. N. C.

**Metabolism of the phosphorus compounds of the acorn during germination in light.** E. Michel-Durand (Compt. rend., 1936, **202**, 866—867).—Analysis of various parts of oak plants about 80 days old showed that P compounds were present mainly in the roots and leaves. The physiological activity of the organs is roots > leaves > stems > cotyledons. J. N. A.

**Effect of insulin on plant respiration.** N. L. Pal and U. N. Chatterji (Nature, 1936, **137**, 535—536).—The leaves of *Hiptage madablota* and *Allium tuberosum* respire at a higher rate when injected with insulin (40 units per 100 c.c.) than when injected with $H_2O$. Phylloclades of *Opuntia Dillenii* show a lower rate of $CO_2$ evolution. L. S. T.

**Chlorophyll fluorescence and carbonic acid assimilation. V. Relation between leaf fluorescence and oxygen assimilation.** H. Kautsky and W. Flesch (Biochem. Z., 1936, **284**, 412—436).—The fluorescence of leaves of *Parietaria officinalis* on ultra-violet irradiation varies with the proportion of $O_2$ in the surrounding atm. With < 0·5% of $O_2$, fluorescence does not increase with increased time of irradiation. $CO_2$ apparently plays no part in the phenomenon. The effect with leaves differs from that of chlorophyll (I) adsorbed on $Al(OH)_3$, the curves indicating dissociation of $O_2$ in the leaf. The rôle of (I), $O_2$, and $CO_2$ in plant respiration is discussed. F. O. H.

**Explanation of the relatively large concentration of $O^{18}$ in the atmosphere.**—See this vol., 698.

**Plant growth in relation to partial pressures of oxygen.** B. N. Singh and G. P. Kapoor (Proc. Indian Acad. Sci., 1936, **3**, B, 238—245).—With increasing $[O_2]$ dry-matter production by wheat plants increases, at first roughly proportionally, subsequently reaching a stationary and finally a declining phase. The initial increase is attributed to a stimulation of assimilation and respiratory processes. The age of the plants is an influential factor. A. G. P.

**Different action of auxin-*a* and of heteroauxin.** J. van Overbeek (Proc. Nat. Acad. Sci., 1936, **22**, 187—190).—The growth-substance curvatures of twice-decapitated *Avena* coleoptiles exposed to visible radiation are < those of non-irradiated controls, when pure auxin-*a* (I) or an extract containing auxin-*a* and -*b* is used; no difference is found when pure hetero-auxin (II) (cf. Kögl *et al.*, A., 1934, 1418) is used. Sections of coleoptiles applied to agar blocks containing (I) or (II) cause destruction of these substances, (I) more rapidly than (II). F. A. A.

**Cell sap acidity and the incidence of white-fly (*Bemesia gossypiperda*) on cottons.** M. A. Husain, A. N. Puri, and K. N. Trehan (Current Sci., 1936, **4**, 486—487).—The gradient in $p_H$ of cell sap from top to bottom of cotton plants varies with type and age of the plant. Incidence of white-fly attack is greater at higher $p_H$ (after a time lag); immunity of some varieties to attack may be due to $p_H$ of sap, and might thus be artificially induced. E. W. W.

**Effect of lead on plant growth.** K. Scharrer and W. Schropp (Z. Pflanz. Düng., 1936, **43**, 34—43).—In sand cultures barley, oats, and, notably, wheat were very sensitive to injury by Pb. Rye and maize were more resistant. Maize was affected by [Pb] > 10 mg. per litre of nutrient. Small concns. had a stimulatory action in some cases. A. G. P.

**Action of sugars on *Saprolegnia*.** F. Moreau (Compt. rend., 1936, **202**, 1086—1087).—Dil. solutions of sugars are toxic to *Achlya colorata* (glucose and fructose > maltose and sucrose). Starch is non-toxic. W. McC.

**Hydrocyanic acid production by leaves of *Photinia*, Lindl.** R. Salgues (Compt. rend., 1936, **202**, 971—973).—The loss of HCN during the period of rapid development attains a max. in September, following which the content rises until midwinter, and again declines until the leaves fall. The life cycle is 20 months. P. G. M.

**Occurrence of cyanogenetic glucosides in S. African species of *Acacia*. I.** D. G. Steyn and C. Rimington (Onderstepoort J. Vet. Sci., 1935, **4**, 51—63).—The glucosides occurred in *A. giraffæ*, *A. litakunensis*, *A. stolonifera*, *A. robusta* (without an enzyme effecting its decomp.), and *A. lasiopetala*. That from the last named (*acacipetalin*), $C_{11}H_{17}O_6N$, had m.p. 176—177, $[\alpha]_D^{22}$ −35·96° and was rapidly decomposed by emulsin. *A. karroo* contained no glucoside. Means of feeding cyanogenetic pods to cattle with safety are described. Ch. Abs. (*p*)

**Composition of pure-bred and hybrid peas.** C. Sosa-Bourdouil (Compt. rend., 1936, **202**, 1091—1093).—The C and H contents of *Pisum sativum*, L., *P. arvense*, L., and *P. Jomardii*, Schrank., of a cross between two varieties of the first, and of crosses between the first and each of the other two exhibit no appreciable differences but the N contents of the crosses (1st—4th generation) are < those of the parent plants. In the crosses there is no direct relation between N content and colour or shape. W. McC.

**Constituents of *Epimedium macranthum*.**—See this vol., 710.

**Heterosides of the fruits of *Sophora japonica*, L.** J. Rabaté and J. Dussy (Compt. rend., 1936, **202**, 1117—1119; cf. Charaux *et al.*, A., 1935, 985, 1041).—In addition to sophoricoside, the pods of *S. japonica* contain rutoside and *sophoraflavanoloside* (I) (yield 0·5%), m.p. 207—208°, $[\alpha]_D$ −61° in EtOH. (I) is readily attacked by emulsin and, on hydrolysis with acid, yields a disaccharide (further hydrolysed to 2 mols. of glucose) and 3 : 5 : 7 : 4′-tetrahydroxy-flavone. W. McC.

**Chemistry and pharmacological action of *Toddalea aculeata*.**—See this vol., 743.

**Saponin of the seeds of *Esculus turbinata*, Blume.**—See this vol., 732.

**Sapogenin of the roots of *Momordica cochinchinensis*.**—See this vol., 731.

**Chemical examination of the bark of *Moringa pteryosperma*.** S. Ghosh, R. N. Chopra, and A. Dutt (Indian J. Med. Res., 1935, **22**, 785—788).—The bark contains a liquid base, $C_7H_9N$ (*hydrochloride*, m.p. 254·4°, $[\alpha]_D^{30}$ +1·8° in $H_2O$), probably a $C_5H_5N$ derivative or an ephedrine base, and an alkaloid, *moringinine*; it also contains org. acids, resins, a phytosterol, fixed and essential oils, and a waxy substance. R. N. C.

**Deltaline, a new alkaloid from *Delphinium occidentale*.**—See this vol., 743.

**Monolupine, a new alkaloid from *Lupinus caudatus*.**—See this vol., 741.

**Isolation of a fourth crystallisable jack bean globulin by digestion of canavalin with trypsin.** J. B. Sumner and S. F. Howell (J. Biol. Chem., 1936, **113**, 607—610).—The *globulin*, obtained by tryptic digestion of canavalin (I), is sol. in $H_2O$ and in 5% NaCl, but insol. in 0·2—1·0% NaCl at $p_H$ 6·5. The isoelectric point, determined by cataphoresis in 0·1*N*-OAc′ buffer, is $p_H$ 4·8. It contains unoxidised S and tyrosine, but not tryptophan. A method for the prep. of (I) from jack bean meal is described. J. N. A.

**Micro-determination of lactic and carbonic acids.** K. Hinsberg and R. Ammon (Biochem. Z., 1936, **284**, 343—346).—Lactic acid is determined in blood (5 c.c.), pre-treated with $CuSO_4$–$Ca(OH)_2$, by heating in a vac. in presence of $MnSO_4$–$KMnO_4$, the MeCHO formed being absorbed in $NaHSO_3$ and titrated iodometrically. Similar apparatus is used for $CO_2$ (liberated by tartaric acid), which is absorbed in 0·2*N*-NaOH, excess of which is titrated by 0·1*N*-HCl in presence of phenolphthalein. F. O. H.

**Spectrographic determination of certain elements by the arc process.**—See this vol., 695.

**Nephelometric micro-determination of chlorine in ash of organic materials.**—See this vol., 693.